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COMMITTEE ON PAPERS AND PUBLICATIONS.

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PAPERS ACCEPTED FOR PUBLICATION:

Methods for the Determination of Manganese. By W. S. Thomas.

The Wet Assay for Copper. By R. S. Dulin.

Acidity of Glucose Syrup and Glucose Sugar. By Horace E. Horton.

A New Hydrogen Sulphide Generator (note). By J. D. Hinds.

A Study of the Behavior of Tungsten, Molybdenum, and their Trioxides. By Charles Hatch Ehrenfeld.

The Tungstates and Molybdates of the Rare Earths. By Fanny R. M. Hitchcock.

On the Reaction Between Zinc Sulphate and Potassium Hydroxide. By C. E. Linebarger.

On Some Experiments in the Anthracene Series. By C. E. Linebarger.

The Determination of Sulphur in Pyrites. A Reply to Dr. Lunge. By T. S. Gladding.

The Zimmermann-Reinhardt Method for the Determination of Iron in Iron Ores. By Mixer and DuBois.

Issued with April Number, 1895.

Proceedings.

COUNCIL.

The following persons have been elected by the Council to serve on the various standing committees for the coming year:

Committee on Nominations to Membership.—A. A. Breneman, P. T. Austen, and C. A. Doremus.

Committee on Finance.—Durand Woodman, A. P. Hallock, and A. H. Sabin.

Committee on Papers and Publications.—J. H. Long and E. F. Smith. Professor Smith desiring to be relieved from duty on this committee, the Council has elected Thomas B. Osborne to the vacancy.

Springfield, Mass., has been chosen as the place for the summer meeting.

NEW MEMBERS ELECTED FEBRUARY 5.

Chesnut, V. K., Bio-Chemic Laboratory, U. S. Department of Agriculture, Washington, D. C.

Cobleigh, Wm. M., E.M., Agricultural College, Bozeman, Mont.

Desper, Ernest W., 37 Shelby St., Worcester, Mass.

Fields, J. W., 88 Wall St., New York City.

Lotz, Dumont, Portland, Ind.

Marshall, Geo. D., care of Newport Mining Co., Ironwood, Mich.

Murray, C. B., Braddock, Pa.

Penniman, Russell S., Lock P. O. Box 26, Dover, N. J.

Perry, Joseph H., 176 Highland St., Worcester, Mass.

Robbins, William K., Amoskeag Manufacturing Co., Manchester, N. H.

Rosengarten, Dr. Geo. D., 17th and Fitzwater Sts., Philadelphia, Pa.

Schloss, Joseph A., care of La Gran Fundision Nacionale Mexicana, Monterey, Mexico.

Thiry, Joseph, care of Dr. G. E. Moore, 221 Pearl St., New York City.

Todd, Albert M., Kalamazoo, Mich.

Viall, William A., Brown and Sharp Manufacturing Co., Providence, R. I.

Woods, Henry, Wellesley, Mass.

ELECTED MARCH 1.

Bogardus, C. E., 60 Columbia St., Seattle, Wash.

Carlsson, Hugo, care of The Johnson Co., Johnstown, Pa.

Cox, W. Wetherill, 2025 Westmoreland St., Tioga, Phila.

Dobbin, Leonard, Chemistry Department, University of Edinburgh.

Dorset, Marion, Bio-Chemic Laboratory, Department of Agriculture, Washington, D. C.

Ehrenfeld, Augustus C., 15 West Monument Ave., Dayton, Ohio.

Ellis, G. H., Metropolitan Block, Chicago, Ill.

Jones, L. J. W., 1821 Arapahoe St., Denver, Col.

Keller, Charles, Wilkinsburg, Pa.

Mixer, Chas. T., 600 East High St., Ishpeming, Mich.

Thompson, Elihu, Lynn, Mass.

Tompkins, Vreeland, 553 Communipaw Ave., Jersey City, N. J.

Wagner, William G., 101 Leadenhall St., London, E. C., England.

ASSOCIATE ELECTED FEBRUARY 5.

Reubens, Charles M., 77 East 115th St., New York City.

CHANGES OF ADDRESS.

Coombs, Frank E., Natick, Mass.

Dewey, F. P., 621 F St., Washington, D. C.

Dodge, F. E., Box 85, Long Island City, N. Y.

Enequist, John, 136 Liberty St., New York City.

Hancock, David, Park View, Portsmouth, Va.

Stone, Edward P., Experiment Station, Durham, N. H.
Townsend, Clinton, Barton P. O., La.
Wrampelmeier, T. J., 909 Steiner St., San Francisco, Cal.

MEETINGS OF THE SECTIONS.

CINCINNATI SECTION.

February 15, 1895.

Dr. Alfred Springer in the chair.

A communication was read from Mr. John H. Westenhoff, stating his inability to be present, on account of a severe cold, and asking to have his paper on "Determination of Phosphorus in Ferro-Silicon" postponed to next meeting.

Professor Norton then stated that Mr. Robert Hochstetter, who was to read a paper on "The Souring of Milk," was detained at home by the serious illness of his business associate, Mr. L. W. Hoffman, and his paper would also have to be postponed.

Professor J. U. Lloyd spoke of the difficulty of obtaining distilled water which would meet the requirements of the U. S. Pharmacopeia, and described the apparatus he was having made consisting of a large copper still, a stone worm forty feet in length, and a stone receiver with stone stop-cock.

Dr. Springer said that absolutely pure distilled water could not be obtained in large quantities for technical use.

Professor Norton told of some interesting experiments carried on at the Laboratory of the University of Cincinnati, for the past five months, to determine the relative value of condensing-tubes made of block tin, aluminum, and glass. He said all glass was affected by water at high temperatures, and water distilled from glass vessels must, necessarily, be more or less contaminated; aluminum, owing to its high conductivity, made an excellent condensing-tube, and did not seem to be affected by water. Condensing-tubes of aluminum could also be used for distilling alcohol, ether, and many other liquids.

Chairman of Standing Committees were elected as follows:

Didactic, Physical, and Inorganic Chemistry, Dr. Alfred Springer, Chairman.

Organic Chemistry, Professor T. H. Norton, Chairman.

Analytical Chemistry, Lewis W. Hoffman, Chairman.

Medical, Physiological, and Biological Chemistry, Dr. S. P. Kramer, Chairman.

Technical and Pharmaceutical Chemistry, Professor J. U. Lloyd, Chairman.

On motion it was—

Resolved, That this Section respectfully recommend to the Committee on Publication of the Journal, the eminent desirability of having the leaves of the Journal cut before being sent to the members of the Society, as is the rule with the publications of the London Chemical Society and the Society of Chemical Industry.

RHODE ISLAND SECTION.

The regular monthly meeting was held at Providence, on the evening of February 23rd. Mr. Frank H. Andrews in the chair. Professor J. H. Appleton read a paper on Argon, presenting the facts as now known, and certain suggestions arising from them.

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THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE SUPERIORITY OF BARIUM HYDROXIDE SOLUTION AS AN ABSORBENT IN CARBON DETERMINATIONS IN STEEL.[1]

BY JAMES O. HANDY, Chemist of The Pittsburg Testing Laboratory, L't'd.

Received January 8, 1895.

THE use of barium hydroxide solution as an absorbent for carbon dioxide is not new. It has long been used for that purpose in air analysis. It has also been used to a very limited extent in carbon determinations in steel.

As an absorption apparatus, Geissler potash bulbs are compact and convenient; they can be used several times without refilling, and are therefore very widely employed. Their use is, however, accompanied by at least one disadvantage; *viz.*, the error caused by differences in the temperature or degree of moisture in the laboratory air at the beginning and end of a combustion. This error sometimes amounts to more than do the small quantities of carbon dioxide whose exact weight it is desired to ascertain. This fact is well known and the error is to a considerable extent eliminated by the following precautions:

(a) Take the last weight of the bulbs from one combustion as the initial weight for the next; if the bulbs have been freshly filled with potassium hydroxide, a blank combustion is always made before taking the weight of the bulbs.

(b) During combustions, keep the bulbs in a covered box and thus shield them as completely as possible from moisture, dust, and heat.

[1] Read at the Boston meeting, December 27, 1894.

(c) Weigh them always at the same interval after finishing the combustion.

In the Pittsburgh atmosphere, fog and smoke are often present. The changes in the degree of moisture are frequently very considerable, even in a few hours. Hence carbon determinations by potassium hydroxide bulbs are especially difficult.

When barium hydroxide solution is used as an absorbent for carbon dioxide it is possible to finish the analysis in at least three ways:

(1) The barium carbonate may be filtered off, washed, ignited, and weighed. This has been done successfully by Mr. Alex. G. McKenna, of Pittsburgh. He uses a special absorption apparatus to which the barium carbonate does not adhere.

(2) The excess of barium hydroxide solution may be titrated:

(a) By a standard oxalic acid without filtering off the barium carbonate, or (b) by standard sulphuric acid after filtering off the barium carbonate.

In either case phenolphthalein is the indicator which is used. I have found difficulty when using the oxalic acid titration in getting a satisfactory end point. With the sulphuric titration, no such trouble was experienced.

The facts that the ratios between C and $Ba(OH)_2$, $BaCO_3$, and H_2SO_4, are so much less than that of C to CO_2.

$$\begin{aligned} C : BaCO_3 &= 12 : 197.4 = 1 : 16+ \\ C : Ba(OH)_2 &= 12 : 171.4 = 1 : 14+ \\ C : H_2SO_4 &= 12 : 98.0 = 1 : 8+ \\ C : CO_2 &= 12 : 44.0 = 1 : 3+ \end{aligned}$$

show the great advantage possessed by the barium hydroxide methods over the potassium hydroxide absorption for carbon dioxide.

When we consider also that the use of standard barium hydroxide and a titration method does away with the uncertain atmospheric moisture factor, it is at once plain that the method has several distinct points of superiority over the potassium hydroxide method.

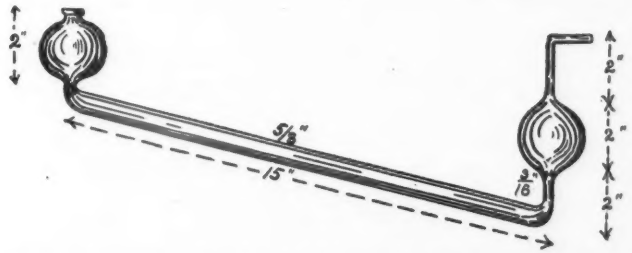
Method for Steels of 0.06 to 0.20 per cent. carbon.—Dissolve, by shaking in a glass-stoppered bottle, ten grams or more of 0.06 per cent. carbon steel or five grams of 0.20 per cent. steel in a mixture of copper and potassium chloride solution, one pound in

1,400 cc. of water, and hydrochloric acid. Use 600 cc. of the former and forty cc. of the latter for ten grams of steel and proportionately, more or less, for other amounts. Filter on asbestos which has been ignited in oxygen, wash as usual, and dry the carbon residue at 100° C. Transfer to combustion tube and make combustion as usual. Regulate the oxygen current so that one bubble starts up the absorption tube just as its predecessor reaches the top.

Between the combustion tube and the absorption apparatus I place only a U tube containing calcium chloride in the first limb and anhydrous copper sulphate in the other.

The absorption apparatus consists of two glass tubes like the one shown in the sketch.

Each tube contains fifty cc. of barium hydroxide solution. Tubes of this shape seem to give the bubbles of gas a rapid rotating motion as they rise through the barium hydroxide solution. As a result, the absorption is very perfect. This is an important point. Many forms of apparatus fail utterly in this particular.



When the combustion is complete and pure air or oxygen has been passed long enough to expel all carbon dioxide, the absorption apparatus is disconnected and the contents filtered.

During the filtration, air purified by bubbling through potassium hydroxide solution is kept playing on the surface of the barium hydroxide solution. This prevents the formation of barium carbonate by the action of atmospheric carbon dioxide on the excess of barium hydroxide. Since laboratory air is often very impure, this precaution is imperative.

The barium carbonate precipitate is washed with distilled water which is free from carbon dioxide. That which has been freshly distilled is best. The water from wash-bottles or flasks is unavailable. When kept in a stock carboy, connected with the laboratory still, I have always found my distilled water free from carbon dioxide. The excess of barium hydroxide solution is quickly titrated after filtering off the barium carbonate and washing it with water free from carbon dioxide.

Standard sulphuric acid is used, with phenolphthalein as indicator. Certain precautions are necessary when filling the absorption tubes with barium hydroxide solution.

By connecting a potassium hydroxide wash-bottle and calcium chloride tube with the blast-pipe, pure air can be easily obtained. Force pure air through the absorption tubes for ten minutes; then close them by rubber connections. While drawing up the fifty cc. of barium hydroxide solution have the pure air current passing into the barium hydroxide bottle. When ready, allow the barium hydroxide solution to run into the absorption tube closing the same again and keeping so until ready to connect with the combustion train.

EXPERIMENTS.

	KOH Method Chemist "L" "C"	$Ba(OH)_2$ method Chemist "H"	Color test KOH standard.
Steel "A" Carbon	0.14	0.134	0.14
" 11834.7 "	....	0.109	0.11
" 11857.0 "	0.17	0.178	0.17
" "M" "	0.08%	0.090 0.093 / 0.091 and 0.092	0.08

STANDARD SOLUTIONS.

Standard Barium Hydroxide Solution.—Twenty grams of barium hydroxide are dissolved in water in a stoppered graduate and then made up to one liter. Filter into a bottle containing pure air, (air which has passed through the potassium hydroxide wash-bottle). Keep a current of pure air playing on the surface of the solution during filtration. It will then remain clear and bright even if the laboratory air is quite impure. Of this solution fifty cc. are more than sufficient for the carbon from five grams of two-tenths per cent. carbon steel. A second absorption tube is usually kept in the train but is rarely necessary.

Standard Sulphuric Acid.—A decinormal solution is used. Of this one cc. = 0.0006 gram carbon.

This method is best adapted for low carbon steels, because only small quantities of barium carbonate have to be filtered and washed.

When analyzing high carbon steels I have used smaller weights of steel (one or two grams) and have rinsed the barium carbonate and excess of barium hydroxide solution into a liter flask; after making up to one liter with pure water, I filter off 200 cc. and titrate by standard sulphuric acid. Steel 11920 gave 1.35 per cent. and 1.35. per cent. carbon by this method.

The work which I have been able to do seems to me to suffice to call attention to the merits of the barium hydroxide methods.

THE CONTRIBUTIONS OF CHEMISTRY TO THE METHODS OF PREVENTING AND EXTINGUISHING CONFLAGRATION.

By Thomas H. Norton.

[*Continued from page 147.*]

The interaction involved the formation of gypsum and aluminum chloride, which, in turn, precipitated the gelatin and converted it into a leatherlike insoluble substance. The object was to fill the pores of the fabric with gypsum and cover the surface with a hard binding material. Sir Frederick Abel, in reporting on the feasibility of this process found that it rendered the canvas very difficult of ignition, but that it also gave to it a degree of rigidity and harshness which forbade its use. In 1856 Maugham[1] patented the use of ammonium phosphate and starch; and in 1857 Thouret[1] patented the use of a mixture of three parts of ammonium chloride and two parts of ammonium phosphate, adopting these proportions on account of cheapness, although the ammonium phosphate alone gave most excellent results.

During this period the importance of better protection for the scenery of theaters was recognized. After a serious fire in the Berlin opera house, the custom was inaugurated of soaking all scenery in a strong alum solution.[2] In 1857 a commission in

[1] Amer. Arch., 13 and 14.

[2] Frémy, *Dict. de Chimie*, 10.

Paris carefully examined the subject, and in accordance with their recommendations the order was issued to have all scenery in theaters impregnated with waterglass.[1] After the lapse of some years it was found that scenery thus treated possessed but slight resistant power. The explanation advanced is that the waterglass, on drying, contracts steadily until the solid particles finally sit very lightly on the yarn of the canvas. Another is that a solvent action is exercised by the water in the water-colors often used by scenic artists. It has been suggested by Hexamer that the impregnation with waterglass could be advantageously followed by treatment with hydrochloric acid, thus precipitating silicic acid directly in the fibers of the yarn, a process practically similar to that of the use of mordants in dyeing.

Versmann and Oppenheim,[2] in 1859, reported to the British Association for the Advancement of Science the results of an elaborate and extended study on the use of salts in treating fabrics, including some forty different substances in the range of their experimentation. Their tests were made on muslin free from starch, weighing 33.4 grams to twelve square inches; and more in the direction of ascertaining the strength of the most effective solution, rather than the weight of a given salt absorbed. After immersion in a solution the excess was removed by pressing and not by wringing. Tests were conducted on a large scale in muslin works and laundries. None of the salts recommended to that time were found available where the operation of ironing was to be performed. Either a smooth surface could not be obtained, or the material was injured on the application of heat.

The valuable results of Versmann and Oppenheim may be briefly summarized as follows:

KCN—very effective in a ten per cent. solution, but poisonous and expensive.

Na_2CO_3 and K_2CO_3—both very effective in a ten per cent. solution, but the one is efflorescent and the other deliquescent.

$NaHCO_3$—very effective in a six per cent. solution, but carbon dioxide is rapidly lost and the protective power disappears.

[1] Frémy, *Dict. de Chimie*, 10.
[2] Loc. cit.

$Na_2B_4O_7$—very effective, but on warming, boric acid is liberated and attacks the fabric.

NaOH—effective in eight per cent. solution.

Na_2SO_4—no effect.

$NaHSO_4$—twenty per cent. solution is protective, but the stuff is gradually attacked.

Na_2SO_3—twenty-five per cent. solution is protective, but the stuff is gradually attacked.

Na_2HPO_4—a saturated solution is effective, but the fabric becomes perfectly stiff.

Na_2SiO_3—the fabric is strongly attacked and the appearance affected.

Na_2SnO_3—protective, but attacks the fabric.

$(NH_4)_2CO_3$—too volatile.

$(NH_4)_2C_2O_4$—renders the fabric combustible.

$(NH_4)_2B_4O_7$—a five per cent. solution gives good protection, but the acid is easily liberated and corrodes.

$(NH_4)_2SO_3$—a ten per cent. solution is very effective, but the salt is deliquescent.

NH_4Cl—a twenty-five per cent. solution gives excellent results, but stiffens the fabric.

$(NH_4)_2HPO_4$—gives excellent results alone or when mixed with ammonium chloride as in Thouret's patent. Maugham's mixture of this salt with starch was not available on account of uneven distribution throughout the mass.

$(NH_4)_2SO_4$—when rendered perfectly neutral by a little ammonium carbonate, this yields the best results of all the ammonium salts. Chevalier's mixture of this salt and borax attacks fabrics at a summer temperature.

$SnCl_2$, $SnCl_4$, $SnCl_4 2NH_4Cl$ } All these are good protectives, but attack the material.

The following salts give good protection when used in solutions of the strength indicated, but are not available on account of price, or corrosive, or other properties; $BaCl_2$, fifty per cent. solution, $CaCl_2$ ten per cent., Al_23SO_4 seventy-seven per cent., $KAl2SO_4$ thirty-three per cent., NH_4Al2SO_4 twenty-five per cent., $FeSO_4$ fifty-three per cent., $CuSO_4$ eighteen per cent., $ZnSO_4$ twenty per cent., and $ZnCl_2$ eight per cent.

Unsuccessful attempts were made to fix upon the fibers such protective salts as $BaSO_4$, $Al_2(PO_4)_2$, and various silicates. Zinc oxide and aluminum oxide gave good results, but would not adhere when washed. Antimony chloride was effective and withstood water, but not soap or soda. Stannous borate, phosphate, and arsenate gave good protection and withstood washing, but gave a yellow tinge to the fabric. Zinc and calcium stannates, while efficient protectors, would not withstand soap or soda. Stannic oxide was fixed permanently but imparted a yellow color. It seemed to be well adapted for coarse material, sail-cloth, canvas, etc.

For light stuffs, to be ironed, sodium tungstate was found to be the best agent, and the most effective solution is one of 28° Tw. or 1.14 sp. gr., containing also about three per cent. of sodium phosphate in order to prevent the formation and precipitation of the acid tungstate.

Where the hot iron is not to be applied directly, ammonium sulphate can be advantageously employed in a ten per cent. solution. The fabric is to be dried in chambers; the ordinary colors on prints, except madder purple, are unaffected.

Versmann and Oppenheim at first sought to produce, artificially, conditions similar to those existing in animal fibers such as silk and wool, which are not inflammable, and which contain about eighteen per cent. of nitrogen. Experiments to incorporate nitrogenous substances such as glue or albumen into vegetable fiber were without practical result, although it was found possible by the use of urea to introduce into muslin thirteen per cent. of nitrogen, rendering it thereby uninflammable.

Essentially the same object is obtained, as we have seen, by the use of ammoniacal salts.

Sir Frederick Abel[1] made reports in 1859 and 1860 to the English Ordnance Department on Versmann and Oppenheim's results, especially with reference to the protection of canvas. The advantages of sodium tungstate for light fabrics were fully confirmed by him. The availability of stannic oxide for sail-cloth was likewise confirmed. Sail-cloth was most effectively deprived of its inflammability thereby, and the protective agent was permanently fixed in the fabric, being affected neither by friction nor

[1] Amer. Arch., 13 and 14.

by repeated washing, while the strength of the canvas was not diminished. The only objections to the use of stannic oxide were: First, the notable increase in weight amounting to fifty per cent. of the original weight of the canvas; and, second, the comparative costliness. While the first objection was regarded by Abel as practically inseparable from the permanent fireproofing of fabrics, the second he considered much more serious. Accordingly, we find him, shortly after, patenting and submitting to the Ordnance Department, a cheaper process for fireproofing canvas, consisting of the deposition in the fiber of a double sodium and lead silicate. Boiling solutions of basic lead acetate and of waterglass were used. I have not been able to ascertain how extended a use was made of this process. Abel in his reports states that he finds saturation with a solution of waterglass alone an efficient protective; but that its value is temporary only. He sums up the difficulties to be encountered in fireproofing fabrics as follows:

(1) The protective material renders the fabric harsh and rigid; or (2) it absorbs moisture and keeps the fabric damp; or (3) it affects the strength and durability of the fabric; or (4) it is easily detached by rubbing or shaking; or (5) it is soluble in water and must be renewed after wetting.

In 1870 Abel[1] recommended to the Ordnance Department treatment with calcium chloride for rope mantelets on board warships in order to keep them damp and prevent ignition during the firing of guns.

In 1871 the Austrian chemist Patera[2] introduced the use of magnesium borate as a protective for fine fabrics and delicate colors. The materials are soaked in a bath of three parts of borax and two and one-half parts of magnesium sulphate in twenty parts of water with the necessary amount of starch, then wrung between cloths and dried. For coarser stuffs he found mixtures of ammonium sulphate and gypsum effective.

In 1882 a special committee of the Franklin Institute of Philadelphia reporting on safety devices for theaters, gave the results of their experiments on the fireproofing of scenery and gauze.[1] They obtained the best results with the material devised by Dr.

[1] Amer. Arch., 13 and 14.

[2] Flammenschutzmittel, Wien, *1871*.

J. Papen, of Frankfort, Germany. The details of its composition are not given, but it has rendered excellent results in the Frankfort opera house, yielding efficient protection, not altering in time, nor affecting the strength or color of the fabrics, and producing no injurious effect on the voices of singers or actors. The committee obtained also very good results from the use of ammonium sulphate, of silica precipitated on the fiber, and from the processes of Gantsch and Judlin, details of which are also lacking.[1]

This question of fireproofing scenery, etc., in theaters had already been the subject of considerable investigation. In 1877 a committee of the House of Commons took evidence on the matter, and we find Mr. Henderson, of the Criterion theater testifying that he used regularly sodium tungstate in the preparation of new scenery; although it was not available for old scenery.

A committee of the London Society of Arts,[1] in 1883, made a report on the same subject, recommending sodium tungstate as the best safeguard for scenery. They found on investigation, that the scenery in nearly all London theaters was treated with some fire-proof preparation; most having as a basis a borate or a silicate. They add in their report: "these compositions do not prevent the evolution of gas when an article is exposed to sufficient heat; and the gas takes fire and burns. When the external source of heat is removed, no more gas is evolved, and combustion ceases. Prepared articles burn when exposed to sufficient heat, but do not support combustion. One effect of this is that it is very much more difficult to set such materials on fire; and this either prevents the breaking out of the fire, or renders it much more easy to deal with when broken out."

The theaters of Paris had already used largely for protecting scenery, a solution of the following composition devised by Martin and Tessier:[2]

Ammonium sulphate	8
Ammonium carbonate	2
Boric acid	3
Borax	1
Starch	2
Water	100

[1] Amer. Arch, 13 and 14. [2] Frémy, *Dict. de Chimie*, 10.

Among recently introduced preparations for the purpose in view, the efficacy of which has not been fully tested, are the following:

Vendt and Herard,[1] 1885. A solution of eight parts ammonium chloride, ten parts ammonium sulphate, two and one-quarter parts sodium thiosulphate, four and one-half parts borax, and seventy-two parts water.

Winckelman:[2]—

Manganese chloride	33 parts.
Glacial phosphoric acid	20 "
Borax	10 "
Magnesium chloride	12 "
Magnesium sulphate	25 "

Fabrics are boiled for six hours in this solution and become thoroughly impregnated with insoluble double salts.

Martin and Tessier:[2]—

Boric acid	6 parts.
Borax	3 "
Ammonium chloride	15 "
Water	100 "

Used chiefly for cordage, sail-cloth, canvas, and straw, the materials being steeped in the solution.

Vogt:[2]—

Ammonium chloride	2 parts.
Zinc sulphate	1 "
Water	20 "
Starch as needed.	

Subrath:[2]—

Alum	5 "
Ammonium phosphate	5 "
Water	90 "

Hattin:[2]—Calcium dihydrogen phosphate, ammonia, and gelatinous silica.

Pereles:[2]—Combined solutions of sodium phosphate, silicate, and tungstate.

Nicoll:[2]—Solution of alum, borax, sodium tungstate, and dextrin, or equal weights of calcium acetate and chloride in hot water.

These comprise the processes for the protection of fabrics introduced up to the present time. As is easily seen, the use of sodium tungstate, the borates, or ammonium salts alone or in mixtures is the striking feature.

[1] *Génie civ.*, 6, 227.

[2] Sc. Amer. Cyclop. of Receipts, p. 217.

A few words with regard to the methods of manufacturing or protecting paper are here in place.

Martin and Tessier[1] used the following bath for paper whether printed or unprinted.

Ammonium sulphate...	8	parts.
Boric acid.....	3	"
Borax.....	1.7	"
Water.....	100	"

The solution is placed in a vat, at the end of the paper-making machine and kept at 50° C.

Paper thus treated is non-inflammable. The value in many kinds of business of a totally incombustible paper is easily appreciated; and several varieties, all based on a large use of asbestos, are in vogue. L. Frobeen's paper is made from ninety-five per cent. of asbestos and five per cent. of wood-pulp mixed in water containing borax and glue. For ink he uses a mixture of platinum chloride and india ink.

Halfpennig's paper[1] is made from one part vegetable fiber, two parts asbestos, one-tenth part borax, and one-fifth part alum, formed in the ordinary way into a pulp to which waterglass is sometimes added. A paper of great flexibility and strength is obtained by coating sheets of linen on both sides with the incombustible paper. His ink is a mixture of graphite, copal, copperas, and indigo sulphate.

Paper is also made from pure asbestos and from asbestos mixed with alum, aluminum sulphate, zinc chloride, and resin soap.

A fire-proof writing-ink is an ammoniacal solution of silver nitrate, with a little india-ink, while platinum chloride mixed with lamp-black and varnish is employed as a fire-proof printing-ink.[1]

METHODS FOR RENDERING WOOD INFLAMMABLE.

In taking up next, the history of the efforts to render wood non-inflammable we encounter two distinct methods of procedure. The first is impregnation by the solutions of the chemical compounds which are to be operative, and includes such variations as the precipitation of insoluble salts within the wood by double

[1] Sc. Amer. Cyclop. of Receipts, p. 217.

decomposition; the second is the covering of the exterior of wood by protective coatings. In the case of existing structures, the latter is evidently the only means available.

The first recorded effort to protect wood was made at Munich in 1823, during the rebuilding of the Royal opera house after destruction by fire.[1] On the recommendation of Professor Fuchs all of the woodwork then received several coatings of waterglass. The surface covered was 400,000 square feet, and the cost was $1,000, or at the rate of $1 for 400 feet. Professor Fuchs prepared his solution by treating ten parts of caustic alkali, fifteen parts of infusorial earth, and one part of charcoal, with water. A somewhat similar composition was also in vogue then in England. It was made by grinding in oil one part of fine sand, two parts of wood-ashes, and three parts of slaked lime, and was applied with a brush. Fuchs' protective kept well, and was regarded as effective for twenty years, but later tests showed that its chemical composition was materially changed, and it no longer afforded security. It may be mentioned here that it was not then found available for scenery on account of the gloss it imparted. During this period the following mixtures came into vogue, chiefly for external protection, as in the case of shingled roofs: three parts of wood-ashes and one part of boiled linseed-oil; three parts of alum and one part of copperas; ashes and lime with skimmed milk as a binding material.

In 1841 Payne[2] introduced his combined process for rendering wood not only uninflammable, but also proof against wet and dry rot and insects. It consisted in the precipitation throughout the mass of a piece of timber, of barium or calcium sulphate by double decomposition. In carrying out the process, wood is introduced into a capacious cylinder, the air is drawn out by steam, and a solution of barium or calcium sulphide is injected into the partial vacuum; the cylinder is exhausted again and then completely filled with the solution of the sulphide; pressure is increased to 140 pounds per square inch, and after an hour the solution is drawn off. The operation is then repeated, use being made of a solution of copperas; as a result the pores of the wood are largely

[1] Rymer-Jones, *Ecl. Eng. Mag.*, **33**, 55, *1885*; Hexamer, *Jour. of the Frank. Inst.*, **114**, 125.

[2] Rymer-Jones, *Ecl. Eng. Mag.*, **33**, 55, *1885*.

filled with the insoluble sulphate and it becomes hard as stone. The soft, porous, cheaper grades of wood are thus rendered equal in point of durability and strength to the hardest varieties of timber. Wood prepared in this way is largely used in England in connection with public works and railways.

[TO BE CONTINUED.]

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY U. S. DEPARTMENT OF AGRICULTURE, SENT BY H. W. WILEY, NO. 12.]

NOTE ON THE ESTIMATION OF IRON AND ALUMINA IN PHOSPHATES.[1]

BY K. P. MCELROY.

Received January 2, 1895.

IN 1888 Dr. Crampton, then First Assistant Chemist of the United States Department of Agriculture, was engaged in the analysis of a lot of baking-powders and did me the honor to entrust to me a portion of the analytical work. Among other things I had to determine the alumina in a number of alum phosphate powders and met with the usual difficulties. By the method I was instructed to use, I found it impossible to get results that were concordant. I therefore systematically went through all the known methods for separating alumina from phosphoric acid and finally decided to use the one accredited to Mr. T. R. Ogilvie in Crookes' Select Methods (page 538, edition of 1886). Briefly stated the method consists in neutralizing the filtrate from the phosphomolybdate precipitate with ammonia, redissolving the precipitate of mixed sesquioxides thus formed, in nitric acid, once more precipitating, filtering, burning, and weighing. The process gave very good duplicate results, and a trial with a known amount of alumina in the form of alum mixed with sodium phosphate gave results sufficiently near theory. This, together with the fact of its having appeared in a work so standard as that of Crookes, seemed sufficient credentials for the method, and I placidly went ahead with its use. When Dr. Crampton prepared his manuscript (which I did not see prior to publication) for his bulletin on baking-powders (Bulletin 13, Part Five, Division of Chemistry, U. S. Department of Agriculture) he gave me credit for the minor modifications I had made

[1] Read at the Boston Meeting, December 27, 1894.

in the method, such as getting the alumina into solution, making up to volume, and the like. As to the main part of the method, the precipitation of alumina by ammonia in presence of molybdate solution, he had as little intention of accrediting it to me as I had of claiming it. He simply said (page 595) that the method "was adapted to the powders by Mr. K. P. McElroy."

Several years later Mr. W. H. Krug of this laboratory was engaged in making an exhaustive examination of a number of phosphate samples and had considerable trouble in determining iron and aluminum. In this connection he tried a number of the current methods on synthetic solutions and got results not agreeing with each other or with theory. At this juncture I suggested that he try the molybdate method. He used it on some phosphates which he had previously examined by the Glaser, Stutzer, etc., methods and obtained much better results. Subsequently he published a paper (*J. Anal. Appl. Chem.*, *1891*, **5**, 671) detailing his work and incidentally he courteously acknowledged my suggestion by saying of the molybdate method that it "was first used in this laboratory by Mr. K. P. McElroy for the estimation of alumina in phosphatic baking-powders." I had also suggested to Mr. Krug some modifications differing in minor detail from those of Ogilvie, by which it would be possible to determine calcium and magnesium in the same portion after precipitation of the iron and aluminum, and these Mr. Krug also published giving me full credit.

For some time since I have known that various chemists had fallen into the habit of calling this method for ferric oxide alumina, the "McElroy method" or "Krug method." Neither of us has taken the trouble to correct this mistake except orally since Crookes' Select Methods is a book of nearly as frequent occurrence in chemical laboratories as Fresenius' Quantitative Analysis, and publishing such a denial of authorship seemed nearly as ridiculous as it would be for one of us to rush into print to announce that he was not the originator of the method for the estimation of sulphuric acid as barium sulphate. Recently, however, a Northern chemist wrote a letter to the Department of Agriculture, designating the method by my name and announcing that in the case of a certain phosphate rock the method had

failed to give results concordant with those of other chemists using other methods. I had always known that the molybdate method did not give results agreeing very closely with those of other methods, but as I had also known that most of these other methods gave incorrect results, I had not laid the fact up against the molybdate method. In view of this specific complaint, however, I have tried the method on known solutions and am astonished to find that it really is liable to lead to grave error.

In this work I tried several samples of the molybdate solutions prepared according to the directions of the Association of Official Agricultural Chemists, which happened to be in the laboratory and found that they gave varying results. The worst results were obtained with a solution made up about six months ago, from which a heavy crystallization has taken place, leaving the residual liquid so weak that it requires over 100 cc. to precipitate the amount of phosphoric acid supposed to be thrown down by fifty cc. of a fresh solution. In two beakers I placed portions of ferrous sulphate representing each 56.4 mgms. of ferric oxide, added a solution of sodium phosphate representing 100 mgms. of phosphorus pentoxide to each, brought into solution in weak nitric acid, oxidized with bromine water, and then precipitated with the molybdate. I washed the precipitate with weak nitric acid and neutralized the combined filtrate and washings with ammonia. The resultant precipitate was dissolved in a solution of ammonium nitrate and nitric acid, filtered, and again thrown down. This precipitate was collected on a filter, burnt, and weighed. The amount recovered was respectively 56.9 and 57.3 mgms., showing a small plus error. In a duplicate set of experiments calcium nitrate equivalent to 400 mgms. of calcium oxide was added to each of the initial solutions. The amount of precipitate recovered in one case was 62.3 mgms. and in another 63.1 mgms., showing a large plus error. During the first precipitation a heavy white crystalline deposit of calcium molybdate occurred. The weighed precipitate was found to contain both lime and molybdic acid, showing that the same phenomenon had occurred in the second precipitation, though it was not visible to the eye.

In each of two beakers were next placed 35.6 mgms. of

alumina in the form of ammonia alum, together with 100 mgms. of phosphorus pentoxide in the form of sodium phosphate and the mixture treated as were those containing iron. The two precipitates of aluminum oxide finally obtained, weighed respectively 28.9 and 29.3 mgms., showing a large minus error. Another set containing 400 mgms. of lime was run through. The same precipitation of calcium molybdate was found to occur. The weights of alumina obtained were but 19.8 and 20.6 mgms. respectively, showing a much larger minus error.

From the above surprisingly bad results it is shown conclusively that the molybdate method for iron oxide and alumina, at least in this form is not at all trustworthy. Yet I have myself at times, and so have others, obtained good results by its use where these results were checked against those made by some of the standard methods used in delicate work.

SOME PRACTICAL POINTS IN THE MANUFACTURE OF NITROGLYCEROL.[1]

By J. E. Bloмén, Ph.D.

Received January 2, 1895.

FROM the very beginning of the commercial manufacture of nitroglycerol the aim of the inventors and manufacturers has been to eliminate the dangers of the operation to the highest possible extent and they have been so successful in this that very few, if any of the many accidents on record can be traced back to the apparatus. The problem is simple enough as the reaction is easily controlled. The indications of approaching danger are clear and the means to avoid it are easily kept at hand. From the old wooden boxes worked by hand with a paddle-wheel to the present elaborate apparatus, the principle is the same—to secure an even and low temperature through the mass of the mixture of acids and nitroglycerol.

It has long been considered that the safest way of stirring is with compressed air, but this can hardly be taken as an axiom. The water, which is formed during the reaction, is of the same temperature as the mixture and does not tend to elevate the temperature, but the moisture brought in with the air certainly does

[1] Read at the Boston Meeting, December 27, 1894.

raise the temperature as soon as it comes in contact with the acid. To prove this point air of the temperature of 82° F. was passed for five hours through a mixture of nitroglycerol acids (three-fifths sulphuric acid to two-fifths nitric acid) of 86° for five hours. After thirty minutes the temperature had risen to 92°, after one hour to 93½°, after two hours to 94°, after three hours to 94¾°, after four hours to 95½°, and after five hours to 95¾°, the temperature of the air remaining constant and the barometric pressure being 762 mm. during the entire experiment.

The apparatus is necessarily far away from the air-compressor and the air therefor has to be carried in pipes for a considerable distance. If then, as frequently happens, the moisture of the air (when not used for stirring) is condensed a considerable quantity of water is forced into the said mixture at one time and it becomes difficult to control the apparatus. Besides a stoppage in the pipe-line may take place at any time—for instance from a bad leakage, from an ice-plug or other substances in a pipe-section, or something may suddenly happen to the air-compressor. For these reasons it is doubtful if this system has any advantage over a stirrer or serpentine screw operated by an engine close at hand and which can be supervised by the operator. The latter way is besides decidedly the more economical as the moisture in the air (most of which comes in at the beginning of the operation) tends to dilute the acid mixture at the time when it is most important that the latter should be as strong as possible and the continuous forcing of warm air through nitric acid cannot but weaken this to a considerable extent.

It is true that when air is used the cooling surface can be better distributed by means of a number of smaller coils through the whole apparatus, but quite sufficient cooling surface is obtained by one big coil (embracing the serpentine screw or paddle-stirrer) when the mixture of the nitroglycerol acids is continually thrown against this and the sides of the apparatus cooled off by a water-jacket.

The question of how big a charge should be used at one time has been a matter of considerable controversy between expert nitroglycerol manufacturers. Of course it would be of the greatest advantage and convenience to use an apparatus big enough

to make one day's output of nitroglycerol in one operation, but this is hardly practical. It seems to be the experience of manufacturing chemists that very few chemical reactions can be effected with advantage on a very large scale; the nearer the operations come to the laboratory conditions the better is the result. This maxim is particularly true in this case. The dilution of the acids by the water formed is considerable — $C_3H_5 - O_3H_3 + 3(H - O - NO_2) = C_3H_5 - O_3 - (NO_2)_3 + 3H_2O$ — and the acid mixture is consequently rapidly weakened. This cannot but have a serious effect on the reaction and if a very big charge is operated the acid mixture necessarily becomes uneconomical in composition. If air is used for stirring, of course, that will also weaken the mixture the longer it is used. Furthermore the acids will always find some little nook or corner of the apparatus—be this of lead or iron—that is weak and in a short time it will act upon it so that the apparatus must be repaired or renewed, and if it then is very big, the trouble and cost this will cause is obvious. Besides, if a charge should need to be drowned, as will happen, the loss is heavy.

On the other hand a charge should not be made too small, because it would take too much time and labor to cool off the acid mixture and rearrange the operation. A convenient charge to operate is one that will take one drum of the acid at a time. One drum holds about (or can by contract be made to hold exactly) 1,500 pounds of mixed acids. Experience has shown that the best composition of acids is three-fifths of the strongest sulphuric acid to two-fifths of the strongest possible nitric acid and 1,500 pounds of this mixture will nearly fill an ordinary iron drum. It has further been proved that it takes a little more than seven pounds of this mixture to each pound of glycerol to obtain a good yield of nitroglycerol. If therefore the apparatus is constructed for a charge of one drum (1,500 pounds) mixed acids and 210 pounds glycerol, it seems to meet the requirements of both practical and theoretical conditions. Of course, the size of the apparatus has to be such as not to allow any undue pressure to be exerted on the charge by confining the mixture and not so large as to allow a play of waste acid fumes to attack a large surface on the top portion of the apparatus.

Of late some so-called continuous apparatus have been proposed. I have never seen one in operation and cannot judge of their practicability. Knowing, however, how difficult it is to get the acid mixture uniform (on account of stratification of the acids), I doubt if they prove economical. If the jets of glycerol and acid mixture meet it is of the utmost importance that the latter should be of uniform composition and the difficulty of getting it so is within the experience of every manufacturer of nitroglycerol. If the acid is not continually stirred it will lack uniformity, and give a low yield, the temperature will fluctuate to a great extent and the danger of the manipulation will be greatly increased. Besides a small jet is easily stopped up and then in a few seconds the point of safety is overstepped.

SEPARATORS.

Formerly, when the cost of the nitroglycerol was of less importance; the nuisance of strongly acidulated water was not considered; and the yield was not all important; the charge was always drowned immediately after it was made. Now it is necessary to recover the "spent" acids, both for the reason of economy and so as to avoid the accumulation of acids, which otherwise would destroy whole tracts of land. On a small scale, when the apparatus only has to be used two or three times a day, it can also be used as a separator, but usually this is not the case, and such a number of separators has to be used as will permit the first one being emptied while the last one is being charged. For this reason the size of a separator ought to be such that it will hold exactly one charge of the converter.

The forms of separators have varied from that of a square box to that of a cylinder and a funnel. As they are generally made of heavy lead it is of advantage to present as few seams and corners as possible, and for this reason they should be made round so that only one seam is necessary. The funnel-shaped undoubtedly possesses several advantages, such as easy separation, but it takes too much space and must be made too deep to be convenient, if the nitroglycerol is to be skimmed off. An ordinary wooden tub, lined with heavy lead (ten pounds to the square foot), which at the bottom has an inclination of about six inches, or is drawn to a funnel-shape, answers the purpose very well.

The faucets of the separators, as well as of the apparatus, ought to be of earthenware, perfectly ground and well greased with vaseline, but the place to put them is hard to determine. The separation line of the nitroglycerol from the acids, varies considerably, partly on account of the difference in yield and partly because the amount of acid used frequently varies from three to four inches.

If the upper funnel be too high up it frequently happens that several inches of nitroglycerol remain and have to be dipped, and if it be too low the amount of acid drawn off would be a source of danger in the wash-house. If the charge is not too big the "dipping off" is accomplished in a short time and the constant stirring of the dipping pan (an enameled iron casserole) in the nitroglycerol helps the separation considerably. It is, however, necessary to have an experienced man in the separating room as the greatest loss is here, if the skimming is not conducted with the most scrupulous care. In most cases it is preferable to dip besides having faucets as every one of them, being brittle as they are, considerably increase the danger from breaking. The separation ought to be accomplished in an hour and a half. If it is not, the glycerol used has been inferior or the operation in the apparatus has been faulty. If the glycerol contains calcium or other alkaline salts and fatty acids there will be found a great number of worm-like particles floating up and down, mechanically carrying nitroglycerol to the acids and *vice versa*, and the charge had better be drowned. The last two inches in the separator should be drowned as it always contains enough acid to considerably raise the temperature of the first wash-water and here is where the funnel, the spout, or the inclined bottom is of advantage as it only allows a narrow separating belt. If the charge is run down in the separator at 17° to 19° C., it scarcely, if ever happens that the temperature rises again to any dangerous degree. It is indeed very rare that it happens that the temperature varies to a dangerous degree in the separators, but it is of the utmost importance to guard against such an occurrence and it ought to be made compulsory for the man in charge to note down the temperature registered at the thermometers in each separator every fifteen minutes, and any neglect

or omission in this respect should be followed by immediate dismissal, as it possibly endangers the life of every one connected with the manufacture.

Before the charge is allowed to leave the separator-house it should be immersed in, and for a few minutes stirred, with cold water, both for the reason of security and economy; of security, because the nitroglycerol mixed with even a small quantity of acid is liable to explode in the pipes in case a friction should take place, or some water be present to raise the temperature of the adherent acid and of economy, because the first wash-water will invariably carry along some nitroglycerol, which ought to go to the drowning tank where it will settle at the bottom of the tank.

WASH-HOUSE.

When it is considered how very important a thorough washing of the nitroglycerol is, what danger a poorly or insufficiently washed nitroglycerol is in the process of manufacture, and that it is an ever-increasing source of danger the longer it is stored, the question of a proper wash-house is one of great importance. As to the form of wash-tubs, the conical one is undoubtedly the best. This form admits the broadest possible surface of contact, it prevents any water coming with the nitroglycerol when it is drawn off, and affords a good opportunity for skimming or drawing off the wash-water. The size need not be larger than to easily accommodate one-half of the charge, because the man who washes has plenty of time to do this when the charges are settling. The wash-tubs as well as the faucets can be of wood (preferably cedar), which should be free from knot-holes, as so little acid comes along when a charge is well separated and has had a preliminary washing in the separator-house that it cannot attack the wood. When a charge is let down the water ought to be let down slowly and from a coil at the side of the wash-tub so as to give it an opportunity to bubble through the nitroglycerol.

If compressed air is to be had, that is, of course, the preferable stirrer, otherwise wooden stirrers can well be used. To prevent waste the wash-water, when drawn off, ought to be allowed to stand in a big tank as it always carries some nitroglycerol along, which will be deposited at the bottom of the tank and should be

taken out at least once a week. The amount of water to be used depends, of course, upon the size of the charge, but twice the volume of the nitroglycerol is certainly enough under all circumstances. If the charge has been well separated and a preliminary washing has been given it one washing will be enough. The last trace of acid should now be taken out. For this purpose a weak alkali solution is used. It is a convenient arrangement to have this solution in a tub set up somewhat higher than the wash-tub and let it run in by gravity, preferably through the coil which is used for the wash-water. If the water in this tub is kept at 30° to 35° C. and the water at this temperature is nearly saturated with sal-soda or if about five pounds of soda-ash are used to about fifty gallons of water the solution is of proper strength. Of this solution I have found that it takes about two pails to remove the last traces of acid in about 460 pounds of nitroglycerol. After the soda solution is drawn off the nitroglycerol should have one thorough washing with water and then it ought to be ready for use. To ascertain this, however, each and every charge should be tested. This of course can be done with any one of the ordinary indicators and the choice of one depends upon the intelligence and education of the man in charge of the washing. For any ordinary workman I would recommend the use of very carefully prepared litmus paper. This is more easily handled than most indicators and is quite sensitive. It must be kept in well-corked bottles and out of the acid fumes. The liquid indicators generally require more skill than the man in charge can be depended on to exercise. Two like strips of litmus paper should be used at one time, one dipped in a little distilled water (which the steam on hand always can furnish) and the other in the nitroglycerol and then be compared. When the wash-water tank is cleaned it will be found that a spongy, dark-gray substance has accumulated. This consists chiefly of salts from alkalies and fatty acids, and holds mechanically a good deal of nitroglycerol. To get this out a felt filter can be used, and by letting it stand long enough in this a good deal of nitroglycerol is obtained.

It is difficult to give a rule for the size of the drowning-tank. This depends upon the size of the converter and the charge used;

the amount and composition of the acid mixture; the size of the separators and somewhat on the temperature of the water available. It must be large enough to allow one full charge to be drowned without the least danger. It would seem as if the larger the tank the greater the safety, but that is not so. If the tank is very big the very large amount of water it holds exerts a pressure, which is likely to spring either the bottom staves or the sides, or the faucets, and if this is done and the acidulated nitroglycerol comes in a crevice not reached by the water, it immediately attacks the wood, generating a heat which sets the nitroglycerol afire and the danger is considerable. It is hard to empty and clean a very large tank; such a tank will last a shorter time than a smaller one, and when it is to be replaced the cost is considerable and the time required, during which the manufacture must cease, is long. On the other hand, if the tank is too small, it is dangerous to drown a full charge; the water in the tank is always strongly acidulated from the last inches of the separators, which must be drowned and is consequently hard to dispose of and constant and tedious cleanings must be made. With these points in view it seems to me to be the best arrangement to have two medium-sized tanks for drowning-tubs connected in such a way that they are in constant communication but will allow each one to be disconnected from the other and connected with the apparatus, separators, and wash-house separately. The size of each one need then only be such that one alone will be enough for an emergency during the short time required to repair the other.

To ascertain the cost of the powder, to be able to check the carefulness of the men, and to rightly regulate the daily output it is of importance that the yield of nitroglycerol and the amount on hand can be easily ascertained at any time. I have found it convenient for this purpose to have the storage tank placed on a large platform scale, where it can be weighed at any time. It is weighed, the amount of nitroglycerol taken out since the last weighing is calculated from the formulas of the powder produced; the weight of tank and nitroglycerol at previous weighing deducted; and this amount divided by the number of charges run down; an average yield will thus be had. The storage tank

—to fit the platform scale—should be a square lead-lined box, and of such a size that it will hold enough nitroglycerol for the manufacture of high-grade dynamite even if three charges should be delayed in converter, separators, or wash-house.

I have found it most convenient to draw the nitroglycerol from the storage tank by means of a rubber hose long enough to reach the top of the tank when raised. If this hose be fastened by a clamp to the upper part of the tank it will not be necessary to have a faucet which must be turned every time a bucket is drawn and which is likely to give rise to considerable friction. By bending the hose sharply between both hands the nitroglycerol will be shut off until the end of the hose reaches the bucket, placed on a small platform scale some distance away, when it can be let down carefully in any desired stream simply by relieving the pressure. The mouth of the hose should, of course, be carefully wiped off before being put back into position.

The problem of conveying the nitroglycerol in the most careful manner from one house to another and from the storage-tank to the mixing-house is one that is astonishingly neglected in most powder works and yet it is one of the utmost importance. It is imperative that no communication by hose, pipes, or trays should exist between the buildings except during the time actually taken to run a charge from one to the other. In case of explosion or fire in one of the buildings the whole factory is doomed to destruction if connections exist between the buildings, but if the connections are cut off the plant can, without difficulty, be so constructed as to make one building independent of the other, as Professor Munroe's valuable experiments have clearly shown, that nitroglycerol is less liable to sympathetic explosion than was generally considered. The converter should be in direct communication with the drowning-tank, and not be allowed, as is so very frequently the case, to communicate with this by the way of the separating-house. This connection may be permanent as the danger of explosion in the drowning-tank is small, but for the sake of additional safety, may be broken near the apparatus. The connection between the apparatus and the separating-house may be made either of lead pipes or rubber hose, but in both cases it should be broken off at an equal distance

from both buildings, a space of at least twelve feet allowed between the ends of the pipes or hose, connection being made between the ends only when a charge is let down and disconnected as soon as the charge is down, and the upper end should terminate in a small lead-lined box to receive drippings. The same conditions should be observed between the separating-house and wash-house, and between the wash-house and storage-tank, and any failure to immediately disconnect the line after use should be severely reprimanded and repetition followed by dismissal. The connecting and disconnecting can be very easily accomplished by a piece of rubber hose and two short glass tubes.

To convey the nitroglycerol from the storage-tank to the mixing-houses pails are almost invariably used. These pails were formerly either of lead or of leather but indurated fiber buckets may be used, if precaution is taken to tare the buckets at least once a week since they are affected to a certain extent by the nitroglycerol.

It is necessary that the nitroglycerol plant with the storage-tank be kept at a considerable distance from the mixing or dynamite manufacturing plant and consequently these buckets have to be carried a long way. The rule not to have any connections between the houses is still more forcible when the connection between the storage-tank and the mixing-houses is considered; no pipe line between the plants should be admissible. In most cases the men have to carry these buckets by hand and a close supervision should be kept to ascertain that the men are careful in doing this, especially in slippery weather. Acting on the suggestion of Professor Munroe some three years ago Messrs. Roebling & Sons built a trolley system to carry the nitroglycerol from the storage-tank to five different mixing-houses at the Forcite Powder Manufacturing Co.'s plant, in Hopatcong, N. J., and this plant worked perfectly satisfactory.

In the construction of a nitroglycerol plant it has always been maintained that it should be so located that the nitroglycerol may run down by gravitation from the converter to the storage-tank. It is well and good if this can be done without inconvenience but it is in no way any absolute necessity, as it can easily

be arranged to press the nitroglycerol from one building to another with compressed air without any great cost and with perfect safety. The mixed acids should, if possible, be cooled off for some time in a place higher than the top of the converter, and if the time it takes to run a charge is allowed for in cooling the acids for the subsequent charge they will not need to be cooled off in the converter, which would otherwise delay the running, considerably. As the glycerol almost invariably has to be warmed before using to assure an even flow and as this operation can easily be done in the converter-house, it is necessary to afterwards press up the glycerol required to a receiver above the apparatus.

The safe distance between the buildings depends partly upon the nature of the ground, partly upon the amount kept in a building at one time, and partly upon the construction of the buildings themselves. The drowning-tank should be as near the converting-house and the separating-house as possible and so low as to assure the rapid discharge of a charge. If the ground is hard the shock of an explosion is more easily carried from one building to another than if it is soft or marshy and the buildings have then to be further apart. If the nature of the ground allows a natural protection of one house from another, or if artificial banks can be built between and at some distance from the houses the latter can, of course, be closer than when unprotected. The buildings ought to be constructed in the lightest possible manner so as to afford little resistance to an explosion, which would otherwise be too powerful. All the buildings must be ceiled and in every way so protected as to assure as even a temperature as possible, but the foundation, the framework, the roof, etc., can be of a very light material. In the separating-house, as well as in the wash-house it is to be recommended that the floor be lined with lead, as this materially assists in keeping the house scrupulously clean and prevents any acidulated nitroglycerol from creeping in between joints, a thing that must be carefully avoided.

To obtain a good yield of nitroglycerol, that is, to make powder economically, the materials selected must be of the best quality or rather of the most suitable quality for the purpose.

To obtain and maintain this there is only one way open to the manufacture; *viz.*, to let a chemist of experience and standing draw up specifications for the acid mixture and the glycerol and to employ a chemist to see that the specifications are rigidly enforced. Some of the more prominent powder works in this country have now such specifications drawn and it would be of great benefit to the trade in general if they should be published so as to lay down a normal rule for the contractors. In this connection I wish to state that whenever it is practicable it is, without doubt, the most economical and best plan for dynamite works to make their own nitric acid. The iron drums, in which the acid mixture comes, are not affected by sulphuric acid but no one ever claimed that they are not affected by nitric acid, and it is hard to see why this should not be the case even when the nitric acid is mixed up with the sulphuric as it can hardly be claimed that the sulphuric acid is a preventive against such attack. It is so frequently lost sight of by manufacturers that the sulphuric and nitric acids are simply a mechanical mixture in which each one retains its peculiar chemical properties, and not a compound different from anything else. This mixture stratifies by standing, the nitric acid corrodes the drums, which are consequently weakened, and, worst of all, it may not be uniform in composition. The contractors frequently mix the acid in tanks in sufficient quantity to fill two or three car-loads. This mixture, which is drawn from the tanks to the drums, must, by necessity, be lacking in uniformity as the specific gravity of the sulphuric acid is so much higher than that of the nitric. It has come within my experience that when the supply of acid mixture was delivered at the beginning of the month instead of being distributed in weekly deliverances, the acid mixture in the drums which have been lying for four weeks has been very much inferior to that which was used in the beginning of the month and that consequently a bad yield resulted. If there were no other reason existing than that of getting a uniform mixture of acids it would be sufficient to advocate the erection of a nitric acid plant, but besides that it is decidedly more economical to have such a plant and it makes the manufacturer more independent both of contractors and of freight service.

To test the stratification of the acid mixture some glass jars four feet high and four inches in diameter were filled with an acid mixture of sixty-five per cent. sulphuric acid to thirty-five per cent. nitric acid and the mixture allowed to stand undisturbed for some time. In four days the color of the upper four to five inches had changed from a pale yellow to a brown color. After six days standing a sample taken six inches from the top had the composition of thirty-eight per cent. nitric acid and sixty-one per cent. sulphuric acid, and after twelve days an analysis gave thirty-nine per cent. nitric acid and 58.4 per cent. sulphuric acid. A sample taken at the bottom of a jar after six days standing gave sixty-eight per cent. of sulphuric acid and thirty-two per cent. of nitric acid, and after twelve days such a sample gave seventy per cent. of sulphuric acid and 29.3 per cent. of nitric acid. These figures represent the average of a number of analyses.

What is to be done with the spent acids and where to run the acidulated water from the drowning-tank and the wash-house are questions which well deserve attention. There exist at present three ways of using the "waste" acids each one of which has some merits. In Europe these acids are most frequently used for the manufacture of fertilizers. Where other fertilizing materials are scarce and insoluble phosphates are plentiful it is natural that the use of this acid for the conversion to soluble phosphate should flourish. The most usual way to utilize the "spent" acid in the United States has hitherto been to "regain" it. The ordinary way of doing this has been to pass the acid mixture through towers filled with coke or bricks where it is met by a jet of steam, which carries the nitric acid through the top of the tower and to receivers, leaving the sulphuric acid to run down to the bottom. The waste of this process is obvious. The sulphuric acid is diluted to such a degree as to make it almost valueless, and the nitric acid rarely acquires a strength of more than 32° to 34° B. The acids in the waste acid mixture has still considerable strength, and to dilute them in order to "regain" them is uneconomical. The third way is to use the mixture direct for the production of nitric acid. It contains nitric acid of the strongest kind, as all the water formed during the reaction has

been taken up by the sulphuric acid, and the sulphuric acid itself has not been diluted to such a degree that it is unsuited for nitric acid manufacture. If the mixed acids, therefore, be added to a charge of sodium nitrate and strong sulphuric acid, almost all of the nitric acid will be recovered. The objection always raised to this plan is that the mixture may contain some traces of nitroglycerol, which would endanger the process. In answer to this it can be said, first, that very little nitroglycerol need be present if the separation has been carefully conducted, and if the acid has been allowed to stand (preferably cooled) for some time before using; secondly, that the very small amount remaining can be exploded by detonating a strong cap in the vessel in which it is stored before using; and thirdly, that even if present in a considerable degree in the retort it would all be decomposed there by the sulphides formed, which are the best decomposers of nitroglycerol known. This way of utilizing the "waste" acid is one of the most economical that can be devised. Unfortunately, however, it only applies to factories having nitric acid works of their own. If the waste acid is kept in iron vessels with free access of air, the vessel will soon be attacked, but if the air is excluded it is not affected. I was brought to this conclusion by observing acid drums a few years ago and to ascertain how far this was true the following experiment was carried on: A small iron still, previously weighed and heated with an iron coil was filled to two-thirds with "waste" acids and connected with a vacuum pump. The acids were now boiled down to about one-half of the still by steam-heat in vacuo. The acid was tested and it was found that the sulphuric acid was of sufficient strength for immediate use and the nitric acid was as strong as before using, but about twenty-four per cent. of the original acid was gone. By adding strong nitric acid to this mixture in such amount as to re-establish the proportion between sulphuric and nitric acids the acid may be directly used again. The still had, after repeated use, lost almost nothing in weight, showing that it was not affected by the acids under this condition. Continued experiments in this direction may give a solution to the problem of how to economically use the waste acids in works which have no nitric acid plant. To pay freight for a strong

nitric acid, use part of it, dilute the rest, and pay another freight back to the factory from where it came, as is done where regaining works are used is certainly not economy.

The acidulated water from the drowning-tanks, wash-house, etc., is frequently a source of great annoyance to the nitroglycerol manufacturers. It cannot be let down into running water as it will soon pollute this; it cannot be run into the field as it will soon destroy all vegetation and cause complaint from all sources. If a deep ravine, separated by considerable earth banks from water supplies is to be found on the ground it may be run into that. The ravine, however, ought to be thoroughly cleaned from leaves, etc., and the bottom scraped so as to enable the soil to absorb the water quickly. If limestone of any kind is to be had on the grounds or near by it is certainly the best way to blast a big excavation, fill it with the limestone, and let the wash-water run into this. The limestone will purify the water from adherent nitric and sulphuric acids and affords a good drain for the water.

How far the risks of the dangerous manufacture of nitroglycerol can be minimized may be judged by the fact that since 1871 no accident of any kind, explosion, or fire has taken place at Winterwiken, Stockholm, Sweden. What is of the utmost importance is to have well-constructed plants, good supervision, and a good chemical knowledge.

COLUMBIAN UNIVERSITY,
December, 1894.

METHODS FOR THE EXAMINATION OF GLYCEROL FOR USE IN THE NITROGLYCEROL MANUFACTURE.[1]

BY G. E. BARTON.

Received January 2, 1895.

THE most commonly accepted methods for the examination of glycerol are described by Allen in his Commercial Organic Analysis, Vol. II.

His requirements are very severe, in fact, too severe it seems to me in some respects. For example, he requires entire freedom from chlorides and iron. Most of the glycerol offered to the

[1] Read at the Boston Meeting, December 28, 1894.

nitroglycerol trade contains both these impurities and, in limited amounts, they are not harmful. He also requires only feeble reaction with basic lead acetate, yet distilled water gives a decided reaction with this reagent.

It is not possible, using the methods of examination Allen gives, to accurately describe a glycerol suitable for the manufacture of nitroglycerol.

The different impurities that such glycerol is liable to contain are:

1. Inorganic bodies, other than sodium chloride, which are shown accurately enough for technical purposes by the ash determination.

2. Sodium chloride.

3. Carbohydrates, sometimes used as adulterants, which are shown by the carbonaceous residue.

4. Fatty acids, either free or combined, a measure for which is found in the total acid equivalent or saponification number.

5. Lighter bodies, mainly hydrocarbons, which influence the permanent specific gravity quantitatively.

The following methods of examination are the result of several years' experience in the examination of glycerol intended for use in the manufacture of nitroglycerol.

Ash and Carbonaceous Residue.—Weigh out between four and one-half and five and one-half grams of glycerol in a tared porcelain capsule and heat cautiously till it inflames. Remove the source of heat and allow it to burn away. Transfer the capsule to a desiccator and, when cold, weigh. This gives the weight of the carbonaceous residue.

The carbonaceous residue ignited gives the ash.

Sodium Chloride.—Take 100 cc. of glycerol, transfer to a porcelain casserole, rinse with distilled water, and add the rinsings to the contents of the casserole. Dilute to 300 cc., neutralize any free acid with sodium carbonate, add normal potassium chromate solution till the contents of the casserole have a decided yellow color, and titrate with tenth normal silver nitrate solution. After deducting two-tenths cc. required to give the coloration, the remainder is calculated to sodium chloride. The weight of glycerol taken is calculated from the number of cubic

centimeters, using the specific gravity at the temperature of the room.

Total Acid Equivalent.—One hundred cc. of glycerol are taken for the determination, transferred to a beaker, made up to about 300 cc., a few drops of a one per cent. solution of alcoholic phenolphthalein added, and then ten cc. of normal sodium hydroxide. Boil for a short time and then run in normal hydrochloric acid till the pink color is discharged. The result is expressed in grams of sodium hydroxide required by 100 cc. of glycerol.

Higher Fatty Acids.—Pass a stream of nitrogen tetroxide through a portion of the glycerol diluted with twice its volume of distilled water, then heat on a steam-bath for two hours. If there is no precipitate formed, either on diluting or later in the operation, the glycerol may be considered free from higher fatty acids. Glycerol intended for use in the manufacture of nitroglycerol should stand this test.

Neutrality.—A glycerol may be considered neutral if, when fifty cc. are diluted with 100 cc. of water and a few drops of an alcoholic solution of phenolphthalein added, not more than three-tenths cc. of normal hydrochloric acid or normal sodium hydroxide solution is required to produce the change in color.

Specific Gravity.—For the specific gravity determination, a Sartorius specific gravity balance is used, and the determination is made at the temperature of the room. The value found is reduced to the value at 15° C. by adding a product represented by $(t-15)$, 0.00065 and subtracting from this sum a number represented by $0.0003+(t-15)\ 0.000025$ R, when t is the temperature at which the work is done, read from a thermometer in the glycerol, and R is the value read from the balance.

Permanent Specific Gravity.—Heat a sufficient portion of glycerol for a specific gravity determination in a 250 cc. flask for two hours, at a temperature between 225° and 230° C. At the end of this time allow the glycerol to come to the temperature of the room, keeping the flask corked with a stopper having a small opening for equalizing the pressure. The specific gravity is then determined as before described. The result is the permanent specific gravity at 15° C.

A good sample for nitroglycerol purposes tested as follows: ash, trace; carbonaceous residue, 0.012 per cent.; sodium chloride, 0.002 per cent.; total acid equivalent, 0.05347; permanent specific gravity, 1.2653; specific gravity, 1.2634; higher fatty acids, none; reaction, neutral.

I am indebted to Dr. Joseph Van Ruymbeke, the inventor of the Van Ruymbeke process of recovering glycerol from soap-lyes, for the first idea of the total acid equivalent and permanent specific gravity determinations.

THE COLUMBIAN UNIVERSITY,
December 17, 1894.

ESTIMATION OF TELLURIUM IN COPPER BULLION.[1]

BY CABELL WHITEHEAD.

Received January 2, 1895.

DISSOLVE from twenty-five to fifty grams of the bullion in nitric acid 32° B. and boil off the excess of acid. Add to this solution an amount of a ferric nitrate solution equivalent to 250 mgms. of metallic iron. Precipitate, while hot, with an excess of ammonia, filter, and wash with dilute ammonia until the copper salts are entirely removed, redissolving and reprecipitating if necessary. The residue on the filter contains the tellurium and selenium present in the bullion as ferric tellurites and selenites. This is dissolved in hydrochloric acid, and excess of tartaric acid added, the solution made alkaline with potassium hydroxide, and hydrogen sulphide passed through it, when the tellurium and selenium pass into solution as soluble sulphides. Filter; decompose the alkaline sulphides in the filtrate with dilute hydrochloric acid; allow the liquid to stand in a warm place until the hydrogen sulphide has been removed. Filter again; dissolve the tellurium and selenium sulphides in aqua regia; evaporate the solution to dryness, take up with hydrochloric acid and precipitate the tellurium and selenium from the solution by passing sulphur dioxide through to saturation. Cover the beaker and allow the solution to stand for twelve hours in a warm place, when the precipitate, which consists of tellurium and selenium, is filtered on a tared filter, dried at 100°, and weighed together.

[1] Read at the Boston Meeting, December 27, 1894.

The selenium is separated from the tellurium by boiling the precipitate in concentrated potassium cyanide solution, filtering, and adding hydrochloric acid, when the selenium comes down as a brick-red precipitate, which is weighed as before, after drying at 100°.

The tellurium is determined by difference or the small amount dissolved by the cyanide solution may be precipitated, after removal of selenium, by saturating with sulphur dioxide, collecting the precipitate with the original residue, and weighing after drying at 100°.

THE COLUMBIAN UNIVERSITY,
WASHINGTON, D. C.

THE USE OF SULPHUROUS ACID ($HNaSO_3$) IN MANUFACTURE OF GLUCOSE SYRUP AND GRAPE-SUGAR.

BY HORACE E. HORTON.

Received January 18, 1895.

UP to the year 1893 a large quantity of the glucose syrup and grape-sugar offered in home markets was manufactured by a carefully worked-out process, in which sulphurous acid had but little if any place.

While a fine grade of glucose can be manufactured without the use of sulphurous acid, its irrational use has taken full possession of some manufacturers.

That sulphurous acid has a legitimate place in a rational process of manufacture few who have studied the subject will deny, but a great deal of careful work is yet necessary to define the use of this reagent.

I have studied the action of sodium bisulphite on glucose syrup and grape-sugar in several directions, and with interesting results. The bisulphite used was manufactured by Gelian and Co., of New York, who have an excellent article of 38°–40° Bé. density.

Preserving Color of Glucose Syrups.—Numerous experiments have convinced me that sulphurous acid is of great value in preserving the color of glucose syrups. I will present here one

experiment, from the many made, to demonstrate this action of the acid.

On June 21st, fifteen batches (ca. fifty barrels each) glucose syrup were manufactured. Batches 2–9 received one gallon 38° Bé. sodium bisulphite and eight fluidounces of muriatic acid; batches 10–15 received two gallons bisulphite and sixteen fluidounces of muriatic acid.

On July 7th, batches 2–9 had lost color and brilliancy. Batches 10–15 of good color and brilliant.

In September batches 2–9 had a *decided* brown color and had lost brilliancy through separation of gypsum (?). Batches 10–15 good color but not brilliant.

In January, batches 2–9 had a *dirty brown* color. Batches 10–15 a *light* straw coloration.

The bisulphite may be added all to the finished product in the cooler, or a part to the liquor in the 39° Bé. vacuum pan, and the remainder to the finished product in the cooler.

The effect of its addition to the 39° Bé. liquor is immediately perceptible in the bleaching of the light straw-colored liquor.

Giving Brilliancy to Candy.—The candy test is for brilliancy and color, and while in some hands gives meaningless results, in skilled hands is a valuable criterion.

This test is carried out as follows: The glucose is weighed into a shallow copper dish along with cane-sugar ("Havemeyer and Elder S. R. Co. 'A' Sugar"), and 150 cc. water added. The proportions of glucose and cane-sugar are the following: For

42°	Bé.	syrup,	8	oz.	glucose	and	1	lb.	9	oz. cane-sugar;
43°	"	"	8	"	"	"	1	"	10	" "
44°	"	"	8	"	"	"	1	"	11	" "
45°	"	"	8	"	"	"	1	"	12	" "

The dish is placed over the direct flame of an eight-inch Fletcher burner and when the mixture begins to boil, five drops of olive-oil are added to prevent trouble from bubbles. Continue boiling for six minutes, watching carefully the rise of temperature with an accurate thermometer, and when 308° F. is reached, which usually requires nine minutes, pour the hot mass on an

oiled marble slab, when it spreads over the surface, making an irregular circular mass of about fourteen inches diameter.

When the mass has cooled sufficiently *to cut*, djvide into halves. Mold one-half into a slab one inch thick, five to six inches long, three inches wide, and wrap in an oiled paper.

The other half is to be cut into strips one to one and a half inches wide, and *without any manipulating*, folded over four times, forming a coil.

From the slab and coil the brilliancy and color are judged. Using a confectioner's glucose made by oxalic acid and run over a dull specially prepared bone-black, a standard candy was prepared having the necessary brilliancy and color.

A large number of glucose samples from sharp bone-black, dull bone-black, specially prepared phosphate bone-black with bisulphite and without bisulphite were made into candy, and in every instance the addition of bisulphite added brilliancy and color.

In connection with candy I must speak of the bugbear sticky candy; there is a great hue and cry attributing sticky candy to the use of bisulphite. I am unable to trace the origin of this assertion to any person, but all are confident of its truth. It may have originated in the practice of preparing syrup for gum-drop manufacturers by adding two and a half buckets of bisulphite and one and a half quarts of muriatic acid to a batch of forty-four barrels 42° Bé. glucose, thus producing an acidity of 0.05–0.055 gram hydrochloric acid in 100 grams syrup. The reasoning may be. If sticky, moist gum-drops are produced by syrup receiving a large quantity of bisulphite, then stickiness and moistness in *all* candy must be due to the use of bisulphite!

I have studied this subject carefully and have been unable to trace sticky candy to the use of bisulphite.

Six samples of candy were boiled using 43° Bé., confectioners' glucose containing two gallons of bisulphite to fifty barrels; six samples of candy using glucose containing eight gallons of bisulphite to fifty barrels.

Three of the candies made from glucose containing two gallons, and three from that containing eight gallons, were exposed

on the laboratory table. Six samples were placed in a closely covered desiccator over sulphuric acid.

It was observed that the samples exposed on the laboratory table grew equally sticky; the samples in desiccator showed no sign of stickiness. This pointed to a certain degree of humidity of the air influencing the stickiness of candy. With this in mind a long series of careful observations were made with reference to the relative humidity of the air, and with the result that stickiness cannot be attributed to the use of bisulphite.

It is interesting to note here, that one candy manufacturer will complain of glucose giving sticky candy, while another manufacturer using glucose from the same batch makes no complaint.

Again, for some unknown reason, it is supposed that glucose receiving over three gallons of bisulphite per batch cannot be used by candy manufacturers for sundry *unknown reasons!* To obtain data bearing on this, batches of glucose were prepared containing five, six, seven, and eight gallons of bisulphite and placed in the hands of a skilled candy manufacturer who knew nothing of the content of bisulphite. In every instance, glucose containing eight gallons of bisulphite gave the best results!

Influence of Bisulphite on Boiling-Point of Candy.—The use of a large quantity of bisulphite makes it possible to boil candy to a higher temperature than when no bisulphite or a small quantity is used.

Batches of confectioners' glucose, 43° Bé. density, were prepared from a sharp bone-black and received varying quantities of bisulphite. Candies were boiled and with the following results:

Batch receiving	2	gals.	$HNaSO_3$	boiled to	308°	F.	Candy good color.
"	"	2	"	"	"	"	330°	"	" very bad color.
"	"	6	"	"	"	"	308°	"	" very good color.
"	"	6	"	"	"	"	330°	"	Color better, but bad.
"	"	8	"	"	"	"	308°	"	Very good color.
"	"	8	"	"	"	"	330°	"	Color improv'g but bad.
"	"	10	"	"	"	"	308°	"	Very good color.
"	"	10	"	"	"	"	330°	"	Color still better.
"	"	12	"	"	"	"	308°	"	Very good color.
"	"	12	"	"	"	"	330°	"	Good color.

In the manufacture of hydrated grape-sugar having the average composition,

Red substance	70.00	per cent.
Water.....	20.00	"
Ash.....	0.52	"
Rest of dextrine.....	....	"
Nitrogenous bodies, etc.	9.48	"
	100.00	

it will be found that liquor from the second filtration can be treated with sulphurous acid to good advantage; and this accomplished by burning sulphur in a small iron furnace and pumping the fumes into the liquor.

Working with an amount of liquor representing 24,000 pounds finished product, the acidity when

½	lbs.	sulphur	is	burned,	is	0.016	gram	HCl	in	100	grams.
1½	"	"	"	"	"	0.027	"	"	"	"	"
2	"	"	"	"	"	0.034	"	"	"	"	"

The use of bisulphite with glucose syrup made it easy to ask the question, What effect will bisulphite have on grape-sugar solutions? Tradition has it that an acidity of over 0.034 gram hydrochloric acid is not allowable; why, no one knows. Some claim that an acidity over this point interferes with the action of the yeast in brewing.

I have experimented in this direction and with the following result:

To batches of grape-sugar sulphured by burning one and a half to two pounds of sulphur and two gallons of bisulphite were added. Laboratory experiments failed to show a diminished activity of the yeast; and more convincing, the brewers using the sugar made no complaint.

It is reasonable to suppose that the slight acidity of 0.034–0.045 gram hydrochloric acid will be taken care of by the calcium carbonate present in water used for brewing.

The addition of bisulphite to grape-sugar solutions led to the interesting observation that crystallization is thereby accelerated. I have made long series of observations and the records clearly show this fact.

I will present a few observations on the subject:

No. of experiment.	Date of manufacture.	Date of observation.	Condition of sample with $HNaSO_3$.	Condition of sample without $HNaSO_3$.
1.	9.12	9.20	Hardened	Liquor on top
2.	9.11	9.20	"	"
3.	9.19	9.20	Heavy cloud of crystals	No cloud
		9.23	Solid	"
4.	9.23	10.4	"	Little syrup
5.	9.23	10.4	"	Considerable syrup
6.	9.23	10.4	"	Little syrup
7.	9.22	10.4	Little syrup	Great deal of syrup
8.	9.22	10.4	Solid	Little syrup
9.	9.22	10.4	"	Moist
10.	9.22	10.4	"	Very little syrup
11.	9.22	10.4	Plenty syrup	$\frac{3}{5}$ syrup
12.	9.21	10.4	Solid	$\frac{3}{4}$ "
13.	9.21	10.4	"	Mushy
14.	9.21	10.4	"	Little syrup
15.	9.21	10.4	"	$\frac{1}{4}$ syrup
16.	6.21	10.4	$\frac{3}{5}$ syrup	$\frac{3}{4}$ "
17.	9.20	10.4	Very little syrup	$\frac{1}{4}$ "
18.	9.20	10.4	$\frac{1}{7}$ syrup	$\frac{6}{7}$ "
19.	9.20	10.4	Solid	$\frac{3}{4}$ "
20.	9.20	10.4	$\frac{3}{5}$ syrup	$\frac{7}{8}$ "
21.	9.20	10.4	Little syrup	$\frac{1}{2}$ "
22.	9.19	10.4	$\frac{1}{4}$ syrup	$\frac{1}{4}$ "
23.	9.19	10.4	Solid	$\frac{3}{4}$ "
24.	9.19	10.4	Solid and dry	$\frac{2}{3}$ "
25.	9.19	10.4	$\frac{7}{8}$ solid	$\frac{1}{4}$ "
26.	9.19	10.4	$\frac{3}{5}$ solid	$\frac{2}{3}$ "

The bisulphite bleaches grape-sugar solutions readily, and its effect on the sugar at the end of fourteen days and after six months is very marked.

Added to the "washer batch" (the batch first dropped from vacuum pan after boiling out with muriatic acid) the effect is pronounced.

TOPEKA, KAN., January 8, 1895.

THE FURFUROL-YIELDING CONSTITUENTS OF PLANTS.

By C. F. CROSS, E. J. BEVAN, AND C. BEADLE.

Received February 13, 1894.

THE chemistry of the formation of the permanent tissue of plants may be approached from various points of view. From the incidents of our working connection with the subject

of cellulose we have, from time to time, dealt with the anterior problem of its elaboration from the point of view of the hexosan complexes which are grouped under this term. De Chalmot, Stone, and others who have followed the pioneering work of Tollens, have been more especially confronted with the relation of the pentoses to plant structure and their life history, and have contributed a very valuable series of investigations now resulting in convincing proofs of important points hitherto of doubtful interpretation.

In the convergence of these two lines of investigation an issue has arisen, and a fundamental problem has become a subject of controversy chiefly between de Chalmot and ourselves.

We have maintained the position:

(1) That the furfurol-yielding constituents of plant tissues are not to be regarded as necessarily and exclusively pentoses or pentosans, since there are oxyderivatives of the hexoses, themselves also C_6 compounds, characterized by the same reactions.

(2) That having regard to the chemistry and physiology of assimilation and cell-respiration in plants, it was probable that the celluloses common with other hexosans would be modified by oxidations of various kinds, these oxidations being probably attended by further combination of the products of oxidation with the parent complex, *i. e.*, with the unchanged residues of the complex.

(3) That, therefore, we may expect to find in the celluloses, furfurol-yielding groups, *not* pentoses.

Upon the subsidiary question as to whether the actual formation of furfurol is not always preceded by a change to a pentose configuration with elimination of the fully oxidized C. position, we expressed no opinion. It is, in fact, altogether irrelevant to the point at issue, which is simply that of the molecules as occurring in the plant tissue.

The controversy has proceeded by stages in the following publications, which we cite in order of time.[1]

The purpose of this communication is to point out, as briefly

[1] Cross, Bevan, and Beadle, *Ber d. chem. Ges.*, **26**, 3520; **27**, 1061; De Chalmot, 27, 1489, 2722.

as possible, that de Chalmot, in his latest communication,[1] closes the controversy in a manner satisfactory to ourselves, although appearing still to join issue with us. It is very necessary to quote two paragraphs from the paper:

(1) p. 589. "*Are there pentosans in plants which are formed from seeds which germinate in darkness?* It has become necessary to answer this question since Cross, Bevan, and Beadle, in a recent article, assert that the furfurol-yielding compounds in the sprouts, which are developed from barley in darkness, are so-called oxycelluloses and are not pentosans."

(2) p. 610. "I wish now to put forward the following hypothesis: Pentose molecules are formed in complex molecules of hexosans (celluloses and hemi-celluloses), in which a part or all of the aldehyde groups have been bound by condensation and are thereby preserved from further oxidation."

This is precisely all that we have contended for. The second paragraph is the answer, from our point of view, to the question contained in the first.

We are dealing, in fact, with an oxycellulose series and the only remaining point at issue between us is this: We are of the opinion that the series is represented in the living tissues. De Chalmot holds that the pentoses are, as it were, explosively formed; the fully oxidized C. group preferring rather a summary exit than the alternative of combining with the basic or alcoholic groups of unaltered hexose or hexosan molecules. This view is, we think, at variance with the perspective of metabolism generally, and certainly contrary to what we know of the chemistry of the oxycelluloses, their very gradual formation under oxidizing treatment, and the intimate union contracted between the oxidized groups and unaltered molecules of the parent cellulose.

Since the final solution of the problem of the constitution of these "natural oxycelluloses" must take the form of quantitative resolution into molecules of simpler, if not the simplest form, it need not be further discussed *a priori*.

We are engaged in a study of their systematic dissection and the results will be communicated in due course.

[1] Am. Chem. J., 16, 589-611.

Of course, it will be understood that these criticisms in no sense lessen the value of the contributions of de Chalmot, and his fellow specialists in the subject of the pentosans, to the general problems of assimilation and metabolism. Any error which may have been made is one only of interpretation. The too free use of "pentose" and "pentosan" as the equivalent of "furfurol-yielding constituents" will prove, we think, to have temporarily obscured some important points in the physiology of the elaboration of plant tissues, but there being now a substantial agreement in the main issue it may well be left to time and experimental investigations to "materialize" this further chapter in the life of the plant cell.

4 NEW COURT, LONDON, W. C.,
January 30, 1895.

THE SEPARATION OF SOLID AND LIQUID FATTY ACIDS.

BY E. TWITCHELL.

Received January 25, 1895.

THE fatty acids insoluble in water, which constitute the greater part of most natural fats, are probably always found as a mixture of two groups, one composed of saturated, the other of unsaturated compounds, the former belonging to the acetic series and the latter to the acrylic and other series containing still less hydrogen. In most fats of commercial importance, such as tallow, lard, cottonseed-oil, and some other vegetable oils, the first named group is represented by only two members, stearic and palmitic acids, which are solid at ordinary temperatures, while the last contains the liquid oleic and linolic acids.

An accurate separation of these groups ought to be the first step in the analysis of any fat, as without it other quantitative reactions, such as the amount of iodine absorbed or alkali combined by the fatty acids, would lead to no very definite conclusions regarding the actual composition of the mixture.

Although a number of analytical methods have been proposed to obtain this separation, their accuracy has not been without question, while in my work I have, at different times, attempted to separate solid from liquid fatty acids and entirely failed to obtain satisfactory results. It therefore seemed to me very

desirable to make a study of some of the methods which have been published, together with any modifications which might suggest themselves in the course of the work. In the following experiments it was attempted not only to compare the different methods, but to determine, if possible, by some direct test, the degree of accuracy of each.

Varrentrapp observed that the lead soap of the solid and liquid fatty acids show great difference in respect to their solubility in ether, soaps of the liquid acids being readily soluble, while those of the solid acids are almost, if not quite, insoluble. On this property of lead soaps have been based the methods which seem to promise the best results, though other solvents than ether have been recommended.

1. Perhaps the most carefully worked-out process is that of Muter, described in the *Analyst* of April, *1889*, which has been employed in examining lard chiefly for the purpose of detecting an adulteration of cottonseed-oil or stearine. This method has been examined and slightly modified by Nathaniel J. Lane, who has published his results in this JOURNAL, February, *1893*. According to this process, the neutral potassium soaps of the fatty acids in boiling water are precipitated by lead acetate. The lead soaps which adhere to the sides of the vessel are washed several times with boiling water, dried as quickly as possible, and then boiled with redistilled ether and allowed to cool thoroughly, filtered, washed, and the filtrate, containing the lead soaps of liquid acids, decomposed with hydrochloric acid and water. The ethereal solution of fatty acids floats on the acid liquid. An aliquot part of this solution is titrated with standard sodium hydroxide to determine the percentage of liquid acids, and another part is evaporated and dried in a current of carbon dioxide and treated with Hübl's solution. Muter finds about ninety-four per cent. as the amount of iodine absorbed by the liquid acids of lard.

Having carefully prepared the insoluble fatty acids of lard rendered in my laboratory (saponifying in the usual manner and decomposing with hydrochloric acid while avoiding exposure to air as much as possible), I carried out the process of Muter, following carefully all important details. A part of the ethereal

solution of liquid fatty acids obtained was put into a weighed Erlenmeyer flask provided with a ground-glass stopper; then dried on the water-bath in a strong stream of carbon dioxide, which had been washed by passing through sodium bicarbonate solution and dried over calcium chloride. After thoroughly cooling the flask, dry air was drawn through for a few minutes to remove carbon dioxide, and the flask weighed. The percentage of iodine absorbed by these fatty acids was then determined in the usual manner, the operation being conducted in the same flask. The object in finding the iodine absorption was to determine, at least comparatively, the purity of the liquid fatty acids, *i. e.*, their freedom from saturated compounds. The following iodine numbers were found:

	Iodine absorbed. Per cent.
Lard	56.27
Fatty acids of lard	58.49 59.26
Liquid acid by above process	94.06

In order to test the solubility of lead stearate and palmitate in ether, a mixture of stearic and palmitic acids, such as is found in commercial stearic acid, was purified by crystallization from alcohol till it gave an iodine number equal to zero. The lead soap was then prepared by the above-described method and a small quantity boiled twice with alcohol to remove free fatty acids and then treated with boiling ether and allowed to cool. At 25° C. 100 cc. of ether dissolve 0.015 gram of the lead soap, and this does not crystallize out at 0° C. This would cause an error of about one per cent. in the above process, while it is possible that, in the presence of lead oleate the solubility of the stearate and palmitate might be much greater.

Another and more serious objection to Muter's method consists in the unavoidable exposure of the lead soaps to the air. All my results seem to show that the lead soaps of the unsaturated fatty acids oxidize even more readily than the free acids. So that, though great care is taken to remove the liquid acids from the air, it does not seem possible to treat lead soaps in this way without a good deal of oxidation, especially during the tedious filtration. Fahrion has noticed this remarkably rapid

oxidation in the case of calcium soaps (*Chem. Ztg.*, *1893*, 17).

2. In his book, Chimie Analytique des Matières Grasses, Jean describes a method of examining lard. This method—modified in the manner of treating the liquid acids—was next employed. Four grams of the same lard fatty acids were dissolved in fifty cc. of ninety-five per cent. alcohol; and to this was added two and a half grams of lead acetate dissolved in twenty cc. of the same alcohol, both solutions being hot. There was an immediate precipitate, and the mixture was allowed to stand one hour at the temperature of the laboratory, and then cooled to 15° C. and kept at this temperature one hour longer. A part was then filtered into a separatory-funnel, treated with ether and dilute hydrochloric acid, washed, and dried in carbon dioxide. The iodine number of these liquid fatty acids was found as in the previous experiment, and their percentage in the original solution calculated. The precipitate was washed thoroughly with ninety-five per cent. alcohol, decomposed with hydrochloric acid, and the solid fatty acids separated and weighed. Their iodine number was also obtained. The following were the results:

	Per cent. obtained.	Iodine absorbed. Per cent.
Solid fatty acids	46.24	4.90
Liquid fatty acids	51.82	103.37

These figures indicate a fractional precipitation in which all the solid and a part of the liquid acids are precipitated. The iodine number of the solid acids and the low yield of liquid acids both point to this. That part of the liquid acids in the solution is probably held there by the acetic acid liberated. This must be the case as lead oleate is only slightly soluble even in absolute alcohol.

If the liquid acids, precipitated along with the solid, consisted entirely of oleic acid as was probable, the iodine number of the liquid part of the fatty acids would be somewhat lower than 103.37 per cent. Yet the amount of liquid acids precipitated being in this case quite small, could only reduce the result by two per cent. at the most. The great difference between this iodine number and that of the liquid acids obtained by Muter's method show that the latter must have contained a considerable amount either of saturated or of oxidized fatty acids.

Jean gives the iodine number of the liquid acids of lard as 92.71. This low figure may be accounted for by the fact that he does not take the precaution to dry the fatty acids in a current of carbon dioxide.

3. It appeared desirable to determine first, whether the liquid acids obtained by the last process were entirely free from solid acids, and second, whether the precipitation was actually a fractional one, more or less of the liquid acids precipitating according to circumstances of temperature, concentration, etc. In order to decide these questions, four grams of lard fatty acids (prepared at another time and from another sample of lard) were dissolved in ninety-five per cent. alcohol and precipitated with lead acetate, cooled for one hour to 15° C., and filtered. Ten cc. of the filtrate were drawn off, decomposed with hydrochloric acid, the fatty acids dried in carbon dioxide, and treated with Hübl's solution as before, while the remainder of the filtrate was cooled for one hour to 0° C. At this temperature there was an additional precipitate. This precipitate was filtered off and washed with ninety-five per cent. alcohol, the washings being thrown away. The fatty acids obtained from the filtrate were also treated with Hübl's solution. The iodine absorbed by the fatty acids of these fractions was as follows:

	Amount obtained.		Iodine number.
Lard fatty acids			62.57
Fatty acids from filtrate at	15° 0.2675 gram	(46.81 %)	109.35 per cent.
" " " precipitate at	0° 0.1020 "		
" " " filtrate at	0° 0.1915 "		118.02 per cent.

The fatty acids obtained from the precipitate at 0° chilled at 0° C. and melted at 7° C. It could therefore contain little or no solid acid, and was probably pure oleic acid. Its iodine number was not determined, but calculating from the iodine number of the filtrate at 0°, it must be very nearly 90—that of oleic acid—to make the iodine number of the mixture 109.35.

It is plain from the above results that the precipitation of fatty acids by lead acetate in alcohol is not a quantitative separation but a fractional precipitation, in which the solid acids are precipitated first, then oleic acid, and finally linolic acid.

Though no quantitative separation of the liquid acids has been

made, their percentage can be calculated as follows: The percentage of liquid acids in the alcoholic filtrate is calculated from the fraction drawn off. This is multiplied by the iodine number of these fatty acids. The result is deducted from the iodine number of the original fatty acids. The difference represents oleic acid. Dividing this by 0.9 gives the percentage of oleic acid precipitated with the solid acids. Adding this to the liquid acid in the filtrate gives the total liquid acid. In the case of the last sample the calculation is: 46.81 per cent. × 109.35 per cent. = 51.19. Deducting from 62.57 gives 11.38. Divide by 0.9 = 12.64, oleic acid in precipitate; add to 46.81 gives 59.45, total liquid acids; whose iodine number is $\frac{62.57}{59.45} = 105.2$.

The linolic acid is easily calculated from the iodine absorption of the liquid acids—109.35 represents 78.5 per cent. oleic acid, 21.5 linolic acid. $21.5 \times 46.81 = 10.06$ per cent. linolic acid in the original fatty acids.

4. A process described by Röse (*Repert. f. analyt. Chem., 1886*) consists in shaking the ethereal solution of fatty acids with finely powdered litharge, when the lead soaps are formed and those of the liquid acids remain in solution. This method was next employed, using not ether, however, but petroleum ether, completely volatile at 80° C., in which I had found lead stearate and palmitate to be much less soluble than in ether. 100 cc. of petroleum ether at 30° C. was found to dissolve 0.0034 gram of the mixed soaps while at 5° only 0.0018 gram were dissolved. Two and a half grams of the lard fatty acids used in the last experiment were dissolved in fifty cc. of petroleum ether, two and a half grams of lead monoxide added, and allowed to stand two hours in a warm place with frequent agitation. A fifty cc. flask was used having a graduated neck. It was filled almost to the stopper in order to avoid the oxidizing effect of the enclosed air. After two hours time the yellow lead monoxide had become white in appearance, due to the formation of lead stearate and palmitate, and the precipitation was judged to be complete. It is clearly not necessary to combine the lead with all the fatty acid. If a part of the liquid acids are in the form of lead soaps this will be a guarantee that all the solid acids have combined. The presence of lead in the filtrate will show

whether the agitation has been continued long enough. Before filtering, the flask was placed in ice-water for half an hour in order to insure as complete a precipitation as possible. Then it was filtered, a definite part of the original volume pipetted off, decomposed with hydrochloric acid in a separatory-funnel, and evaporated and dried in a current of carbon dioxide as before. The liquid acids calculated to the whole solution yielded 55.10 per cent. having an iodine number of 108.66. The precipitate on washing then decomposing with hydrochloric acid gave 44.70 per cent. solid acids having an iodine number of 3.02 per cent. This impurity was probably caused by an oxidation of the liquid acids to compounds whose lead soaps were insoluble in petroleum ether.

The results obtained here are not far from those calculated by the alcohol method. The petroleum ether method would have the advantage over the other in that the iodine number would be that of the liquid acids and not only of a fraction from which part of the oleic acid has been precipitated. On the other hand a quantitative result by the petroleum ether method could only be arrived at where the fat is perfectly fresh and the greatest precautions have been taken to avoid oxidation during the whole manipulation. The same sample of lard fatty acids, after standing seven days in a closed jar, gave the following results:

	Iodine number.
Solid acids.....	10.1 per cent.
Liquid "	101.7 "

The oxidation had given products both soluble and insoluble in petroleum ether; and in this case the percentage of liquid acids cannot be inferred from the analysis.

A precipitation of all the solid and part of the liquid acids by lead acetate in alcohol, by the method described by Jean, with the addition I have proposed of finding the iodine number of both the original fatty acids and those in the solution, and calculating therefrom, would give accurately the percentage of solid and liquid acids in a fat. Such a method would perhaps be too cumbersome for general commercial work. Still I believe it is at present the only positive solution of the problem.

IMPROVED METHODS OF WATER ANALYSIS.

By Irving A. Bachman.

Received January 2, 1895.

WE have in the South Atlantic States incontestable evidence that the true source of malarial disturbance is to be found in the water, and not in the air, as was formerly supposed. The introduction of deep-seated artesian wells has very materially decreased this trouble, and has rendered localities that were notoriously unhealthy, perfectly healthy.

The examination into the exact difference between the malaria-producing waters and those proof against it, has had the writer's attention for over two years, and the work herein detailed is a portion of the preliminary work looking into the best methods of analysis.

My experience with the Wanklyn process as ordinarily carried out with the usual apparatus, so impressed me with its crudeness, that for a long time I have had little confidence in the results I obtained. The loss by imperfect condensation, the crude way of adding the permanganate solutions, and the open-air contamination of the distillate are by no means in keeping with accurate work. The loss by imperfect condensation is very much greater than we permit ourselves to believe, and with the original Wanklyn process[1] is a very difficult matter to control; the loss is variable, and is dependent upon the rate of distillation and the efficiency of the cooling apparatus. After making a long series of experiments upon every character of material liable to be found in water, I am satisfied that a rate exceeding fifty cc. in fifteen minutes is accompanied by loss. As a modification of the Wanklyn process, Mallèt[2] proposes to keep the original volume of liquid in the retort constant by the systematic addition of ammonia-free, distilled water, in order to prolong the action of the permanganate; this is objectionable, inasmuch as the operation is endangered by a constant source of error in the addition of ammonia-free water, which is difficult to obtain in so large a quantity.

[1] Wanklyn and Chapman Water Analysis, (6th ed.), *1884*, pp. 38–40.

[2] Report National Board of Health, *1882*, p. 210.

In my own work I had frequently noticed that the evolution of ammonia very often increased as the liquid in the retort became more concentrated.

Acting on this observation it occurred to me that by the action on a smaller and limited quantity of water by the full strength of the permanganate solution and supplying the water under examination at about the rate of distillation, very much better results could be obtained; this I have now confirmed by a great many comparative analyses.

The apparatus used is shown in Fig. 1, and consists of distillation flask A, of one liter capacity, into which is fitted by a ground joint the remainder of the apparatus (this is the only

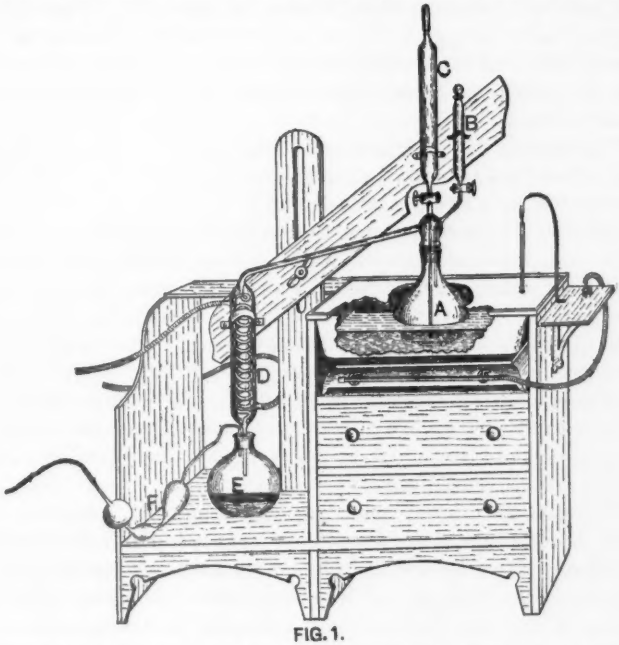


FIG. 1.

connection the apparatus has); through the bulb of the neck we have two burettes with stop-cocks, the smaller, B, with a capacity of fifty cc., with its tube projecting within three inches

of the bottom of the distillation flask; the larger burette C, has a capacity of 250 cc. and its tube projects to within one-half inch of the bottom. The cooling apparatus D, is a closely coiled glass worm, with a long projection at the lower extremity, to which is attached the distillate vessel E, by a soft rubber stopper, which also has tube for connection with the Will and Varrentrapp absorption bulb.

The apparatus is constructed to work under greatly reduced pressure, and the connection with distillation flask, as well as the stop-cocks, are accurately ground to remain tight without a lubricant.

The apparatus is mounted as shown, raised and lowered into the bath by means of a thumb-screw, as indicated. The whole is very easily managed, and is very serviceable. I have made over a thousand determinations with mine, and there is no reason why it will not continue to do good service for a very long time to come.

The heating of the apparatus is effected by setting the flask into a fixed saline-bath, with a covered top as shown, and heated from below by a two-pipe gas-burner.

Mode of Procedure.—After thoroughly rinsing the apparatus with ammonia-free distilled water, 500 cc. of the water under examination are put into the flask and the apparatus connected and lowered into the bath, the distillate flask with Will and Varrentrapp bulb, the latter previously charged with Nessler solution, are now attached and connected with the pump.[1] The partial vacuum is now established gradually, the sodium carbonate solution added by way of the smaller burette, and the distillation started and continued until 200 cc. have been distilled over, which is then nesslerized for free ammonia.

The vacuum tube is now disengaged and the stop-cock on large burette opened and about 250 cc. of the liquid in the distillation flask drawn up and the fifty cc. of alkaline permanganate solution, previously poured into the smaller tube, is now allowed to run in after the distillate flask has again been attached.

[1] Richards is an excellent device, but it is important to have a small check-valve in the tube to prevent the water being drawn into the apparatus when the water pressure is suddenly diminished. A very simple valve is made of oiled silk opening only toward the pump.

We now have fifty cc. of alkaline permanganate acting on fifty cc. of water, and after, say thirty to forty cc. have been distilled over, the water in the large tube is allowed to drop in at the same rate as the distillation, which must not exceed fifty cc. in fifteen minutes. [The rate of distillation, as recommended by the Chemical Section of the American Association for the Advancement of Science, *i. e.*, fifty cc. in ten minutes, is too rapid, and is very frequently accompanied by loss by imperfect condensation; this is very readily observed in my apparatus by discoloration of the Nessler solution in bulb.] The distillation is continued until 250 to 300 cc. have been distilled over, which is then nesslerized.

The following notes from my laboratory work will show the general plan of the work:

One gram urea was *dissolved in one liter* ammonia-free water.

1. Ten mgms. urea in 300 cc. of ammonia-free water, 250 cc. drawn up into tube, fifty cc. permanganate solution added, bath 87° C., cooling water 28° C., pressure six and a half inches, distillation at rate of 150 cc. per hour, 310 cc. distilled over with slight discoloration of Nessler bulb. 30.2 : 2.0 :: 310 : 2.053 mgms. ammonia, or 20.53 per cent. which is 36.2 per cent. on ammonia obtainable.

2. Five mgms. urea in 300 cc. ammonia-free water treated as above—297.4 cc. distilled over, no discoloration of Nessler bulb. 28.8 : 1.0 :: 297.4 : 1.032 mgms. ammonia, or 20.64 per cent. which is 36.4 per cent. on ammonia obtainable.

3. Ten mgms. urea in 300 cc. water, 250 drawn up, fifty cc. permanganate solution added, bath 85° C., cooling water 27° C., pressure five inches, rate of distillation, 100 cc. per hour, 290 cc. distilled over, no discoloration of Nessler bulb.

25.1 : 2.0 :: 290.0 : 2.310 mgms. ammonia, or 23.10 per cent. on 40.7 per cent. on ammonia obtainable.

4. Ten mgms. urea in 500 cc. water, ten cc. strong solution sodium carbonate added, bath 87° C., cooling water 28° C., pressure five and a half inches.

210 cc. distilled over as free ammonia, which yielded 0.835 mgms. ammonia or 8.35 per cent.

250 cc. were then drawn up, fifty cc. permanganate solution added, and distilled as before.

305 cc. were distilled over, which yielded 2.296 mgms. ammonia, or 22.96 per cent.

Total ammonia 8.35 per cent. free, plus 22.96 per cent. albuminoid, or 31.31 per cent. which is 55.2 per cent. on ammonia obtainable.

Rosaniline hydrochlorate yielded	86.02	per	cent.	on	ammonia	obtainable.
Strychnine sulphate	" 78.10	"	"	"	"	
Urea-boiling five hours	" 79.90	"	"	"	"	
Cyanuric acid	" 61.10	"	"	"	"	
Quinine sulphate	" 77.09	"	"	"	"	
Morphine sulphate	" 81.11	"	"	"	"	

The apparatus, Fig. 1, is also used for the Kjeldahl process. This process was first described for use in general water analysis by Drown and Martin,[1] and is now very generally used in place of the Wanklyn process.

I have modified the Kjeldahl process so as to insure more perfect decomposition, and have obtained most gratifying results with the most obstinate organic compounds.

Process.—300 cc. of the water under examination is put into the distillation flask of apparatus already described (Fig. 1) and the whole connected up; ten cc. specially prepared concentrated sulphuric acid is allowed to drop in slowly by way of the smaller burette, the whole is then allowed to digest at 85° C., under diminished pressure for, say one hour, and then brought to a boil, and so continued until the contents are colorless. The acid is then neutralized and the solution rendered strongly alkaline by the addition of fifty cc. strong solution of ammonia-free, sodium hydroxide through the smaller tube.

250 cc. of the contents are then drawn up into the larger tube and fifty cc. of permanganate solution added through the smaller tube, and the distillation carried on as already described in the modifications of the Wanklyn process, and nesslerized as before.

The modified process combines the good features of the Wanklyn and Kjeldahl, and is easily carried out with the apparatus described. The original sources of error are now practically eliminated.

The following are some results upon some of the substances

[1] Technology Quarterly, 2, 3.

that with the Wanklyn process yield only a very small percentage of the ammonia. I have made no comparative tests with the original Wanklyn process, and quote Mallet's:[1]

	Mine.		Mallett, by Wanklyn's Process.				
Rosaniline hydrochlorate	96.9	per cent.	23.8	per cent of theoretical amount.			
[2]Cyanuric acid (distillation two hours)	89.1	"	2.1	"	"	"	"
Cyanuric acid (distillation four hours)	91.2	"					
Urea (from urine).....	100.3	"	22.2	"	"	"	"
Urea (from ammonium cyanate).....	99.0	"	20.8	"	"	"	"
Potassium ferrocyanide	59.8	"	none	"	"	"	"

In nesslerizing I have found the Leed's Comparator modified as in Fig. 2, best suited to my wants. The work is very much facilitated by having one tube with stop-cock carefully graduated up to 100 cc., and connected to another tube, as shown in Fig. 2;

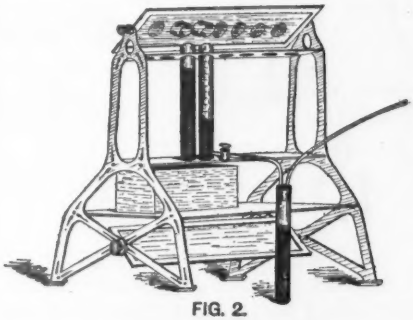


FIG. 2.

by using the blowing tube the liquid can be raised or lowered at will, and compared with the known solution with a nicety and exactness that I have been unable to attain by any other plan.

Combustion Process.—The Frankland combustion process[3] is entitled to more general use for regular work on water analysis; in my hands it has yielded satisfactory results after eliminating the objectionable features of open-air evaporation.

[1] Report Board of Health, page 253-254.
[2] After standing over night yielded 1.7 per cent. additional.
[3] Frankland: Water Analysis, London, *1890*.

The apparatus designed for this purpose is shown in Fig. 3, and is constructed to hold a vacuum of fifteen mm. for four hours after pump has been stopped. The vessel A is set into a fixed table water-bath, to a depth of two inches, and the water under examination, in closed reservoir, B, the capacity of which is 200 cc., is admitted into A by a tube of very fine bore, and the vapor of water carried over into the sulphuric acid absorption col-

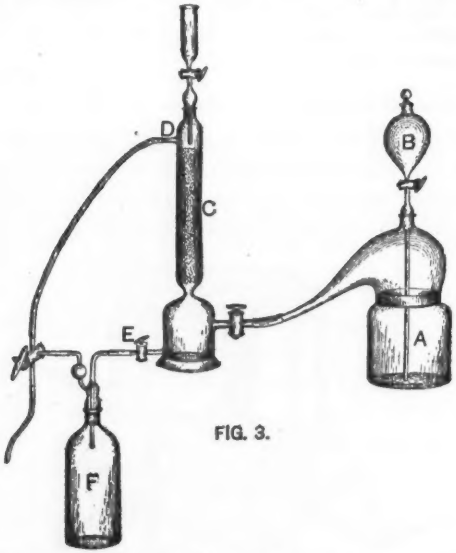


FIG. 3.

umn C, which is filled with broken glass tubing and has travelling through it, pure concentrated sulphuric acid. The vacuum tube to jet-pump is connected to the upper, D, and lower, E, connection of the absorption column by a three-way cock, by which the operation is momentarily suspended and the vacuum held, while the acid accumulated in the lower part of the column is drawn into a bottle, F, by diminished pressure.

Concentrated sulphuric acid is such a powerful absorbent that under the vacuum produced by a good jet-pump, ice can be readily and rapidly formed in the vessel, so that with the water in the bath at 30° C., the evaporation is rapid; actual boiling,

however, must not be permitted. The water is admitted only at the rate of evaporation which can be adjusted to a nicety by the stop-cock. Care must be taken to start the pump cautiously, thereby establishing the vacuum gradually, and to have only a thin layer of water in the vessel to avoid serious spattering in the escape of the bubbles of gas. In this way 500 cc. of water is evaporated to dryness in six to seven hours, and requires little or no attention after the apparatus is once adjusted.

The following comparative experiments have been made on water:

PARTS PER MILLION.

	Wanklyn.	Wanklyn with my modifications and apparatus.	Kjeldahl, Drown, and Martin.	Kjeldahl with my modifications and apparatus.
	Free and albuminoid ammonia.		Organic nitrogen calculated as ammonia.	
Savannah river at Augusta	Free, 0.011 Albu., 0.130	Free, 0.010 Albu., 0.165	0.172	0.175
	0.141	0.175		
Savannah river, at 26 feet	Free, 0.180 Albu., 0.135	Free, 0.183 Albu., 0.236	0.421	0.420
	0.315	0.419		
Well water, Summerville	Free, 0.092 Albu., 0.116	Free, 0.105 Albu., 0.186	0.285	0.287
	0.208	0.291		
Spring water supplying Hotel Bon Air	Free, 0.015 Albu., 0.123	Free, 0.018 Albu., 0.209	0.205	0.219
	0.138	0.227		
Driven well, below Augusta	Free, 0.685 Albu., 0.605	Free, 0.700 Albu., 0.976	1.855	1.867
	1.290	1.676		
Driven well in So. Carolina	Free, 0.416 Albu., 0.395	Free, 0.422 Albu., 0.566	1.116	1.121
	0.811	0.988		
Artesian well water, Georgia Chem. Works	Free, 0.005 Albu., 0.036	Free, 0.005 Albu., 0.042	0.050	0.050
	0.041	0.047		
Distilled water with 10 per cent. of water from pool in garbage pile	Free, 0.620 Albu., 1.136	Free, 0.653 Albu., 2.251	3.007	3.100
	1.756	2.904		

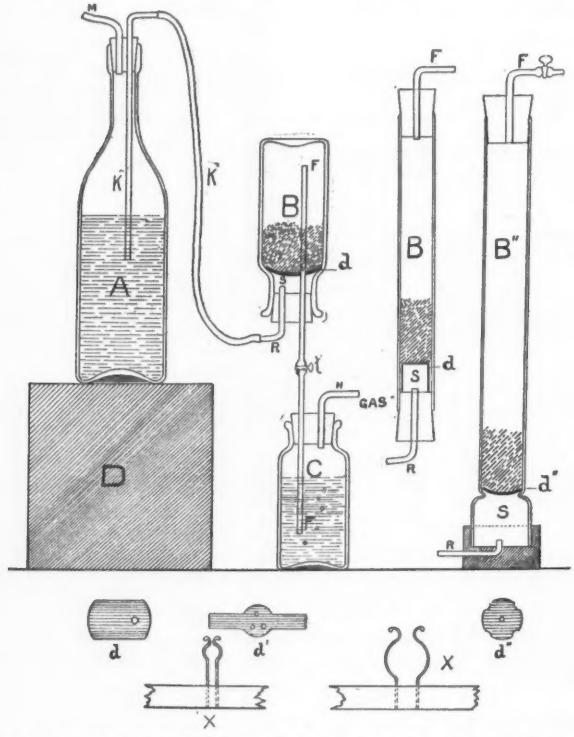
AUGUSTA, GA., December, 1894.

A CHEAP FORM OF SELF-REGULATING GAS GENERATOR.

By W. W. Andrews.

Received February 6, 1895.

THIS form of generator is so cheap and easily set up that it makes it possible for every teacher and experimenter in chemistry to have, at practically no expense, a set of generators



capable of yielding, whenever called upon, a supply of hydrogen, hydrogen sulphide, chlorine, carbon dioxide, sulphur dioxide, etc. It consists of an ordinary bottle, A, to serve as reservoir

for the acid, a smaller bottle, B, which is the generator proper, and C, the familiar wash-bottle. A is closed by a cork holding two pieces of glass tubing. The one M just pierces the cork and the other, K, reaches down a short distance below the surface of the acid and is connected by means of a rubber tube with R, thus forming a siphon leading from A to B, as shown in cut. The tube M is used to start the siphon KR by blowing into A while the stop-cock, *f* is open. F is the exit tube for the gas. The charge of solid in B rests on a shelf of sheet lead, *d*, the width of which equals the diameter of the neck of the bottle, and its length the internal diameter of the bottle. It serves the purpose of securing a space, S, which prevents the extra gas generated, when *f* is closed, from pressing the acid out of the siphon. Instead of a bottle for holding the charge a calcium chloride tube, or an Argand lamp chimney, with its larger end closed with a cork or sunk into a wooden block and cemented with paraffin wax, or even a piece of large-sized tubing may be used. If the last be used the space S is secured by cutting the lead in the shape *d'* and bending it to form a bench to support the solid charge, as shown. d'' is the shape of the lead support to be used in the calcium chloride tube or Argand chimney. x and x', are the wire springs for holding B to its support, from which it may be lifted or replaced instantly. One is to enclasp the body and the other the neck of the bottle, or one of the glass tubes below the cork.

The advantages of this form of generator are:

1. Its cheapness. An ordinary fruit-juice bottle and two wide-mouthed eight-ounce bottles will, with the necessary tubing, make one of good capacity.

2. Its convenience and safety. It is strictly self-regulating. If a rubber tube fitted with a glass plug one-half inch long, instead of a stop-cock be used, the gas flows only when the fingers pinch up the rubber along one side of the plug and ceases the moment they are lifted. The apparatus, therefore, is self-closing. It is very easy to recharge either with acid or solid.

3. It ensures a more even quality of gas than the well-known Kipp, and as complete utilization of the acid as the Koninck generator. When the gas presses the acid back from B, it enters A laden with dissolved solid and, on account of its greater specific gravity,

it falls in a straight line to the bottom, where it spreads out in a dense layer. When the apparatus is again set working, the purest acid is drawn from the upper layers. There is, consequently, some advantage in using a tall bottle for A.

4. It may be put together in a form which has all the advantages possessed by the Schanche generator (see this JOURNAL, Dec. *1894*.) Making the glass tube R, long enough to reach to the top of B, and to curve a little downward, so that the acid may drop on the top of the solid charge and trickle through it. A drainage-tube with stop-cock must be inserted into the cork to carry off the used-up acid from the space S. The inverted bottle for B, possesses this advantage over the calcium chloride tube or chimney; *viz.*, that owing to the position of the mouth of the gas exit tube F, solid particles are not so likely to be shot into it when the acid is vigorously attacking the solid charge.

5. The pressure can be regulated at will by placing A at different heights, and this pressure may, at any moment, be reinforced by blowing into A, and the reinforcement held by closing M by means of a rubber tube and pinch-cock.

SOME OF THE PROPERTIES OF CALCIUM CARBIDE.

BY F. P. VENABLE AND THOMAS CLARKE.

Received February 7, 1895.

THE calcium carbide used was prepared by the Willson Aluminum Company. In this preparation, lime is mixed with some form of carbon, as coal-tar; the mass is then heated, with stirring, until a thorough mixture is obtained. The proportions are so arranged that the mass becomes dry and hard on cooling. This mass, in lumps, is then placed in the electric furnace. In a very short time after the turning on of the current, the process is complete. The molten mass can be run out of the crucible or it may be removed after cooling. On examination, it is easy to see that there is more or less of carbon unchanged, or rather converted into the graphitic variety by the intense heat. Along with this are to be seen crystalline masses, lustrous and dark brownish black in color.

These are quite hard, and break with a crystalline fracture. Several efforts at effecting a separation from the graphitic carbon

were unsuccessful. The luster is slowly lost on exposure to air, more rapidly if the air be filled with moisture. The whole will finally crumble down into a gray powder with particles of black graphite interspersed through it. The carbide can be kept for a year or two if placed in a tightly stoppered bottle and is quite easily preserved if a little coal-oil is placed in the vessel containing it.

By far the most interesting property of this carbide is its decomposition when brought in contact with water. The metallic carbides seem to be distinguished by the ease with which they exchange their carbon for the oxygen of water or for the radicals of various acids, the carbon combining with the hydrogen to form various hydrocarbons. Several authors have reported that the decomposition of this particular hydrocarbon caused the formation of acetylene. Experiments were carried out by us proving this fact, some time before there were any publications concerning it in the chemical journals, but we were not at liberty to publish anything concerning it at that time. If the gas, as evolved, is passed through a set of absorption flasks containing ammoniacal copper solution it will be entirely absorbed, not a bubble passing through, out of one or two liters of the gas. Thus it seems to be pure acetylene. The amount of gas yielded by any one sample will be affected to some extent by the amount of graphitic carbon present. Hence different lots will vary somewhat. The average is about 200 cc. to the gram of carbide.

If the gas be ignited as it is evolved it gives a smoky flame; if it be considerably diluted, as one part of gas to from six to ten of air, a flame of great brilliancy and intensity is gotten. A company has been formed to introduce this as an illuminant upon the market. The cheapness of the materials used and the ease with which the gas can be formed ought to make it a valuable and useful addition to our illuminants. If too large a proportion of air be admixed a very violent explosion can be brought about by igniting it. In some cases we have noticed the flame rapidly travelling backwards along a rubber tube towards the gasometer in which the gas was stored. One explosion taught us that care was necessary in handling the mixture.

Several analyses were attempted of the carbide, but for obvious

reasons failed to give very satisfactory results. In the first place there was uncombined carbon present, also a small portion of a tarry matter which could be detected by heating to high temperatures, and lastly, the specimens worked upon were several months old and in spite of careful keeping, had been slightly acted upon by the air and so contained uncombined lime or calcium carbonate. Moissan gives C_2Ca as the formula calculated from his analyses. This would agree well with the decomposition by water; $C_2Ca + H_2O = C_2H_2 + CaO$.

Action of Hydrogen upon the Carbide.—Dry hydrogen has no action upon this carbide in the cold. Several small pieces of the carbide were placed in a piece of combustion tubing, drawn out at one end to a point suitable for testing the flame. Dry hydrogen was then passed over it and as soon as the air was expelled the hydrogen was ignited at the jet and a lamp placed under the tube so as to heat the carbide. In a little while the colorless flame became luminous and remained so a short time. A brownish tarry matter condensed in the cooler parts of the tube. The mass of the carbide assumed a dull gray tint and a very thin white sublimate collected at a short distance from where the tube was heated. The ignition was carried on for five hours. The driving off of this tarry matter seemed to be the only action. The substance on removal from the tube, was still hard. On exposure to the air, it disintegrated, and, if thrown into water, it was decomposed, showing the same behavior as the original carbide.

Action of Air and of Oxygen.—Some fresh pieces of the carbide were placed in the tube and heated while dry air was passed over them. A luminous flame was gotten as before and the same tarry matter was driven off and then there seemed to be no further action. Tests showed the carbide apparently unchanged at the end of prolonged heating.

Oxygen was then passed over some of the carbide which was being moderately ignited. No change was observed after two hours' heating. If the temperature was very high, such as that gotten in a cumbustion furnace, the carbide glowed brightly, as if burning, and a nearly white powder was obtained. The combustion was imperfect, however, unless the tube was very hot and the ignition prolonged. This refers not merely to the gra-

phitic carbon mixed with the carbide but to the carbide itself. In several experiments the substance withdrawn from the tube, after heating some hours in oxygen, decomposed violently in water. It may be added, as was to be expected, that carbon dioxide had no appreciable action upon the carbide.

Action of Hydrochloric Acid.—Hydrochloric acid had no action upon this substance in the cold. When passed over the heated substance it caused it to swell up and assume a dirty gray appearance. A small amount of a liquid, apparently water, collected in the cooler portions of the tube and parts of the carbide fused down in glassy globules and masses. These were soluble in water and were easily shown to be calcium chloride. White fumes were evolved some of which settled as a white solid upon the sides of the tube.

Action of Chlorine and Bromine.—When chlorine was passed over fresh carbide in the cold no action was observed. If even a moderate heat was applied, however, the lumps of carbide glowed very brightly, swelled, and fused together. A slight yellowish white sublimate was found in the tube. The fused mass was calcium carbide.

Bromine mixed with air was then passed over the fresh carbide. In the cold no action was observed. On heating, the carbide became red and the smaller pieces glowed. The lumps fused together and bubbles were observed on the surface as if some gas was escaping from the mass. Some condensed matter was found afterwards in the tube, and, on cooling, a peculiar odor was noticed different from that of bromine. The fused mass dissolved readily in water and gave the tests for calcium bromide. Of course in this and the previous experiment the black specks of graphitic carbon were found unchanged. It was easy to distinguish them from the carbide. A few pieces of the carbide were dropped into strong, freshly prepared, chlorine water. There was a very violent disengagement of gas but it was not ignited as reported by Moissan. The gas was inflammable and burnt very much like acetylene. The odor was, however, peculiar. The same experiment was tried several times with a concentrated solution of bromine in water. The action again was very violent but there was no spontaneous ignition of the gas.

Little difference could be detected between this and the action of the chlorine water.

Action of Acids.—A piece of the carbide was placed in concentrated pure sulphuric acid. A few small bubbles came off but the action seemed slight. On heating, the action was greatly increased and continued after the removal of the flame. A gas was given off which burned with a luminous flame.

A mixture of sulphuric acid and potassium bichromate acted most violently upon the carbide. There seemed to be a very vigorous oxidation, and several attempts at igniting the gas given off resulted in failure. There could have been very little, if any, acetylene present in it.

Strong nitric acid attacked the carbide with the formation of brown-red fumes. The gas evolved could be ignited and burned with a smoky flame.

Glacial acetic acid decomposed the carbide slowly in the cold.

It may be added that no change was observed on adding a piece of the carbide to some boiling sulphur. On allowing the mass to cool the carbide was regained in its original condition.

Action of Alkalies.—A few grams of sodium hydroxide were melted in a nickel dish and a piece of the carbide was added. There was violent action, a gas being given off which burned with a luminous flame and which was taken to be acetylene.

A small amount of sodium dioxide was also melted in a nickel dish. When the carbide was added to this it was rapidly attacked, the action being about the same as in the experiment just mentioned. An inflammable gas was evolved.

In conclusion, we would give due credit to Mr. W. R. Kenan, who carefully verified some of the experiments here recorded.

UNIVERSITY OF NORTH CAROLINA,
February, 1893.

NOTE ON THE DETERMINATION OF ZINC.

BY P. W. SHIMER, EASTON, PA.

Received January 24, 1895.

THE manganese in many zinc ores is a disturbing element in the accurate determination of metallic zinc. As is well known the usual separation of zinc from manganese is made by precipitating the zinc as sulphide in a solution which is strongly

acidified with acetic acid. When the manganese is high this precipitate should be dissolved and reprecipitated to purify the zinc sulphide from a little manganese sulphide thrown down with it. To avoid this troublesome reprecipitation I have lately used the following method which does away with the disturbing influence of manganese, and gives results agreeing closely with those obtained by the usual methods.

About eight-tenths gram of the zinc ore is dissolved as usual in hydrochloric acid. In case, as often occurs, there is any insoluble manganese or zinc spinel in the residue, it is necessary to make a fusion. Evaporate the hydrochloric solution to dryness and redissolve and filter if it is desired to determine the silica. In case silica is not to be determined it need not be filtered off. Redissolve in nitric acid (1.20) and evaporate to moist dryness. Add 100 cc. strong nitric acid and precipitate the manganese as dioxide by means of potassium chlorate, as in Ford's method for manganese in iron and steel. Filter through purified asbestos by means of the filter-pump and wash, first with strong nitric acid, then with cold water. Dissolve the manganese precipitate in standardized ferrous sulphate solution and titrate the excess of ferrous sulphate with standardized permanganate solution as in Williams' method for manganese in iron and steel. In this way the manganese is promptly separated, and if desired, determined.

The filtrate from manganese is transferred to a beaker and evaporated to dryness. A little hydrochloric acid is added and again evaporated to moist dryness. On this solution the usual double basic acetate precipitation is made. The united filtrates are evaporated to a bulk of about 300 cc., heated to boiling, removed from the flame, and a rapid current of hydrogen sulphide passed through for one-half hour. The zinc sulphide is filtered off and dissolved in hydrochloric acid and the zinc precipitated, preferably as zinc ammonium phosphate. The precipitate is separated from the paper and weighed as zinc pyrophosphate. The ignition should be done cautiously at a low red heat to avoid fusion of the pyrophosphate and a probable cracking of the crucible at the moment of solidification. In case lime is to be determined in the filtrate from the zinc sulphide, it is

necessary to dissolve and reprecipitate the calcium oxalate, for the first precipitate is sure to contain alkaline chlorides in very appreciable amount. The basic acetate precipitate cannot be used for the determination of alumina, since the manganese precipitate carries down a little iron with it, but apparently no determinable amount of zinc.

ON THE DETERMINATION OF CANE-SUGAR IN THE PRESENCE OF COMMERCIAL GLUCOSE.[1]

By H. A. Weber and William McPherson.

IN the analysis of a great many of the saccharine products found in the markets at the present time, the chemist is confronted with the problem of determining sucrose in the presence of commercial glucose. The official methods for such determinations, either by the use of Fehling's solution alone or supplemented by the polariscope, necessitate, as is well known, the inversion of the sucrose by the action of acids. The accuracy of these methods requires, as one condition, that the acid used in inversion exert no action upon any substance present, other than sucrose, that would in any way affect the reading of the polariscope or would change the power to reduce Fehling's solution. Since commercial glucose, however, contains a greater or less amount of dextrin, and since this undergoes hydrolysis when acted upon by acids, being changed thereby into dextrose, the question arose as to whether such a change might take place during the process of inversion of any sucrose present and thus vitiate the results. The specific rotatory power of dextrin being nearly four times as great as that of dextrose, it is evident that a very slight action would introduce serious errors.

The method of procedure was, first, to determine to what extent dextrin is present in commercial glucose; second, to ascertain whether any change is produced by heating with acids as in the common process of inversion, and finally to discover some method of eliminating this error, if present.

[1] This paper and the one following were sent to Dr. H. W. Wiley to be read before the Association of Official Agricultural Chemists and then transmitted to the editor of this Journal for publication. In consequence of a misunderstanding they were printed instead, in the Proceedings of the Eleventh Annual Convention of the above association. At the request of the authors, and with the consent of the Committee on Papers and Publications, they are now reprinted in full.—Ed.

An examination of the literature accessible upon the subject of the composition of American glucose failed to give any information in regard to the amount of dextrin present.

The report on glucose, Washington, 1884, gives the analysis of some glucoses, but as suggested by Stone and Dickson,[1] improvement or variation in the manufacture since that time would probably cause a change in the chemical composition.

In order to obtain the desired information a number of samples were analyzed. Seven of the samples were kindly sent us by the American Sugar Refining Company, of Chicago, and represent the various grades placed on the market by them. Since this company controls the glucose manufacture in the United States, it is fair to presume that these samples represent, more or less fairly, an average glucose in the market. Two other samples were purchased in Columbus, but analysis showed a composition similar to those sent from Chicago, and inquiry revealed the fact that they had been purchased from the above-mentioned company.

METHOD OF ANALYSIS.

A number of different methods have been proposed for the estimation of the constituents of glucose, all more or less objectionable. The shorter ones are only fairly approximate, making no attempt to estimate the amount of the so-called inert or unfermentable carbohydrates (gallisin). The longer methods are probably more exact, but, since the unfermentable carbohydrates are but imperfectly known, it follows that any attempt at finding the exact composition cannot be highly satisfactory.

The following method[2] was selected as giving approximately the relative amounts of dextrose, maltose, and dextrin present.

Twenty-five grams of the glucose were dissolved in water, and the solution made up to 250 cc. With this solution the following determinations were made:

1. *Specific gravity.*—This was determined by weighing with the pyknometer. The Westphal balance was first used, but the results were not so satisfactory as those obtained by direct weighing.

2. *Specific rotatory power.*—This was deduced from the direct

[1] *J. Anal. Appl. Chem.*, 7, No. 6.

[2] See article Sugar, Thorpe's Dictionary of Applied Chemistry.

reading in a 200 mm. tube. The instrument used was the ordinary Schmidt and Haensch polariscope. Its accuracy was tested by a standard plate, kindly loaned by Dr. Wiley.

3. Cupric reducing power.—A gravimetric determination was made by adding ten cc. of the solution properly diluted to forty cc. of Fehling's solution previously heated in boiling water until it attained a like temperature and then heating for twelve minutes in water at 100°. The cuprous oxide was filtered through asbestos, well washed, and changed into the cupric form by igniting for fifteen minutes. The weight of the oxide multiplied by 0.4535 gives the amount of reducing sugar present. Experiment showed that good results could be obtained by exercising due care and adhering rigidly to the conditions.

4. Ash.—Fifty cc. of the solution were treated with sulphuric acid in a platinum dish until all the carbonaceous matter was burned away, the residue weighed, and the percentage of ash calculated.

The total organic solid matters per 100 cc. were determined by subtracting from the specific gravity of the solution (water = 1,000) the correction due to the ash, and dividing the difference between the result and 1,000 by 3.86. This is based on the assumption that ten grams of carbohydrates dissolved in 100 cc. of water give a solution of sp. gr. 1,038.6 (water = 1,000), also that one gram of ash per 100 cc. gives a specific gravity of 1,008. Now, if in a solution containing ten grams to 100 cc.,

S = total carbohydrates,
(A)d = specific rotatory power for ray D,
K = cupric reducing power in terms of dextrose,

then

$$\text{Maltose (M)} = \left(\frac{(A)d + 1.42K - 195}{27.2}\right)S$$

$$\text{Dextrose (D)} = \frac{SK}{100} - 0.61\ M.$$

$$\text{Dextrin} = S - (M + D).$$

It is evident that this method will give only approximate results, since it supposes that the only organic bodies present are maltose, dextrose, and dextrin. However, the results undoubtedly give a fair insight into the amounts of these present.

TABLE NO. I.—GLUCOSES ANALYZED.

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Specific gravity	1030.60	1031.05	1031.40	1031.18	1033.16
Total solids, grams	7.8890	8.01	8.08	8.03	8.56
Specific rotatory power	133.33	132.90	120.60	135.40	132.10
Ash, per cent	0.18	0.19	0.24	0.21	0.17
Cupric reducing power, per ct.	56.56	57.00	60.60	54.90	56.70
Maltose, per cent	54.08	55.44	34.63	54.20	55.40
Dextrose, per cent	11.64	11.81	21.24	11.03	14.71
Dextrin, per cent	13.18	12.80	24.98	15.09	15.44
	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Specific gravity	1033.90	1031.17	1031.48	1033.50	.....
Total solids, grams	8.74	8.00	8.11	8.60	.....
Specific rotatory power	127.80	149.30	130.31	134.91	40.20
Ash, per cent	0.22	0.37	0.29	0.37	.....
Cupric reducing power, per ct.	55.90	43.60	50.65	48.75	.....
Maltose, per cent	39.12	47.67	22.30	28.92	.....
Dextrose, per cent	25.08	5.81	27.48	24.31	.....
Dextrin, per cent	23.18	26.52	31.33	32.81	.....

It is of interest to compare these results with the following, the first three of which are taken from the report on glucose above mentioned. The fourth is the analysis published recently of a product manufactured in England.

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.	No. 4. Per cent.
Maltose	19.3	7.6	....	36.10
Dextrose	36.5	36.5	39.0	18.75
Dextrin	29.8	40.9	41.4	25.41

The most noticeable feature of the above analyses is the high per cent. of maltose present and the comparatively low per cent. of dextrose. With a single exception the maltose present exceeds the dextrose, reaching a maximum difference in number 7, which contains 47.67 per cent. maltose and only 5.81 per cent. of dextrose. This particular sample was labeled "Brewers' Extract," the name suggesting a high per cent. of maltose, a characteristic property of the glucoses obtained from Chicago with a malt-like odor noticeable when dissolved in a slight amount of hot water. It will be noticed that the English sample contains almost twice as much maltose as dextrose.

The solid glucose or grape-sugar was not analyzed completely, since the specific rotatory power was so low as to exclude any possibility of the presence of dextrin.

It is of interest to compare the properties of the above glucoses with those examined by Stone and Dickson.[1] The determinations made by them were, in the main, different from those made by us, overlapping, however, in the determination of the specific rotatory power and ash. A marked difference exists in these. The average specific rotatory power of those examined by Stone and Dickson is given as 91.37, while those examined by us showed a variation from 120.6 to 149.3, calculated for ray D. It is possible that the former calculations may have been made for some other ray, and the apparent difference thus diminished. The percentage of ash in the samples examined by us was noticeably smaller, being about one-fourth as great.

The glucoses were next subjected to the same treatment as would be necessary to invert sucrose, if present, *viz.*, heating with acids. It is evident that in order to guard against any hydrolysis of the dextrin or to diminish it, if unavoidable, the temperature to which the acid solution is raised as well as the time during which this temperature is maintained should be no greater than necessary to insure complete inversion of the sucrose. Various methods of inversion have been proposed and various ones are in use by chemists at the present time. The official methods of the agricultural chemists for the years 1890 and 1891 require that the solution to be inverted, mixed with the proper amount of acid, be heated for ten minutes at 68°. This was changed in the report for 1892 and continued in the report for 1893, to heating gradually, reaching 68° at the expiration of ten minutes. This is also the method given by Allen,[2] as well as the one recommended by the "Association des Chimistes."[3]

Three different methods were tried: 1. The above-mentioned or official method; 2. The method recommended by the Association of Official Agricultural Chemists for the years 1890 and 1891, *viz.*, heating at 68° for ten minutes; 3. The German method, which amounts to heating at 67° to 70° for fifteen minutes.

Approximately 26.048 grams of glucose were dissolved in 200 cc. of water. Fifty cc. of this solution mixed with five cc. fuming

[1] *J. Anal. Appl. Chem.*, 7, No. 6.
[2] Allen's Commercial Organic Analysis.
[3] Jour. des Fabr. de Sucre, 32, *1891*, No. 35.

hydrochloric acid were heated according to the above-mentioned methods.

TABLE NO. II.—READINGS OF AN APPROXIMATELY FIFTY PER CENT. SOLUTION OF THE VARIOUS GLUCOSES, BEFORE AND AFTER HEATING WITH ACIDS. TEMPERATURE, 20° C.

[Divisions on cane-sugar scale.]

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.	No. 10.
Direct reading 200 mm. tube	85.70	85.50	80.10	86.55	85.30	84.40	90.40	84.90	86.15	42.00
Reading after inversion by first method	85.20	84.85	79.58	86.00	84.90	83.90	89.85	84.20	85.55	42.05
Difference	0.50	0.65	0.52	0.55	0.40	0.50	0.55	0.70	0.60	....
Reading after inversion by second method	84.25	83.90	78.75	85.15	84.00	82.90	88.95	83.00	84.45	....
Difference	1.45	1.60	1.35	1.40	1.30	1.50	1.45	1.90	1.70	....
Reading after inversion by third method	83.75	83.20	78.10	84.60	83.50	82.15	88.35	82.25	83.75	....
Difference	1.95	2.30	2.00	1.95	1.80	2.25	2.05	2.65	2.40	....
Reading after boiling one hour with acetic acid (com.)	85.30	84.90	79.75	86.15	84.85	84.05	89.90	84.30	85.65	....
Difference	0.40	0.60	0.35	0.40	0.45	0.35	0.50	0.60	0.50	....

The flasks were carefully calibrated and the duplicates agreed within the error of reading. The results are given in the above table. The solutions were of such a strength that the amount used was the same as would be used in the analysis of a substance containing approximately fifty per cent. glucose.

It will be noticed that in every case, with the exception of No. 10, which contains no dextrin, the reading is sensibly diminished, introducing thereby an error in the estimation of sucrose in the presence of commercial glucose, varying from one-tenth to over two per cent., according to the amounts of the two present and the method of inversion used. While this may not be large enough to cause one to draw unjust conclusions from the analysis of commercial saccharin products, it is nevertheless desirable to eliminate it if possible, or at least to reduce it to a minimum.

Experiments were made to find out the effects of other acids in the hope of finding one that would bring about the inversion without affecting the reading of the glucose. The result showed, however, that even an acid which would not bring about complete inversion would sensibly diminish the reading of the glucose. Thus acetic acid will cause a diminution of reading almost as large as that caused by hydrochloric acid, although it does not *seem* to cause complete inversion. In no case was a smaller error introduced than by the first method above used.

Since the error could not be eliminated by inversion with acids[1] an attempt was made to allow a correction for it. It is evident from the above results that the error is not a widely diverging one, if the samples can be regarded as average ones, and it could be largely diminished by allowing for the mean deviation.

It was necessary, however, before attempting this to find out what the effect would be when the amount of glucose present was varied. Solutions were made containing, approximately, 100, 50, 25, 10, and 5 per cent. of glucose, respectively, and subjected to the action of acids as before. The average results expressed as divisions on cane-sugar scale, were as follows:

	100 per cent.	50 per cent.	25 per cent.	10 per cent.	5 per cent.
Before.....	170.7	85.00	42.35	16.8	8.6
After.....	169.4	84.45	42.15	16.78	8.65
	1.3	0.55	0.2	0.02	....

The results with the various glucoses are sufficiently uniform to warrant one to introduce corrections which, while not eliminating the error, would reduce it to a minimum.

This correction may be easily calculated as follows:

It can readily be seen that the reading due to glucose present may be approximately determined by subtracting from the direct reading three-fourths of the difference between (or sum of) the direct and invert readings (supposing that the temperature be about 20°).

[1] This error would be eliminated by the inversion brought about by O'Sullivan and Thompson's invertase process (*Journal of the Chemical Society of London*, 59, 46). The method is not used to any extent, however, because of the time required as well as the increased labor of analysis.

Let R equal the reading due to glucose, then the following formula deduced from a graphic representation of the above results will be found to give the correction (x):

$$x = \frac{R - 15}{130}$$

This correction must, of course, be subtracted from the numerator ($a \pm b$) in Clerget's formulas. In order to test the accuracy of the above correction a number of mixtures of cane-sugar and glucose were analyzed. Good results were obtained in every instance. The following expressed as divisions on cane-sugar scale, will serve as examples:

Glucose. Per cent.	Sucrose. Per cent.	Direct reading.	Invert reading.	Approximate glucose reading.	Correction.	Per cent. of sucrose found: Without correction.	Per cent. of sucrose found: With correction.
80	20	154.2	126.30	133	0.90	20.82	20.18
50	50	138.4	70.75	87	0.55	50.48	50.11
30	70	120.3	26.23	50	0.27	70.20	70.00
10	90	109.0	11.80	19	0.03	90.15	90.13

The results in Table No. 11 show the necessity of chemists using the same method of inversion. Even in the estimation of pure sucrose it has been shown by a number of chemists that the reading varies slightly according to the method used. In the presence of commercial glucose, however, the variation becomes much greater. When the inversion is accomplished by heating at 68° for ten minutes, the difference in reading due to the hydrolysis of the dextrin averages almost three times as great as when the first method is used, while the German method increases this to almost four times. It is barely possible that some of the widely varying results published by the reporter on sugar, in the report of the Association of Official Agricultural Chemists, may owe a part of their discrepancies to these facts.

CONCLUSIONS.

Some of the conclusions reached may be summarized as follows:

(1) An error is introduced in the estimation of sucrose in the presence of commercial glucose, due to a slight hydrolysis of the dextrin present during the process of inversion of the sucrose by acids.

(2) This hydrolysis, and consequently the error, is reduced to a minimum when the inversion of the sucrose present is effected by heating for ten minutes, the temperature being gradually raised so as to reach 68° at the expiration of this time.

(3) The results with the different glucoses are sufficiently uniform to warrant the introduction of a correction for the mean error.

(4) In order that the results may be comparable, chemists ought to strictly adhere to one method of inversion.

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ON THE ACTION OF ACETIC AND HYDROCHLORIC ACIDS ON SUCROSE.

BY H. A. WEBER AND WILLIAM MCPHERSON.

WHILE carrying out some experiments with glucose several facts were noted in reference to the action of acetic and hydrochloric acids on sucrose, which it is interesting to compare with the conclusions reached by Bornträger,[1] Jungfleisch and Grimbert,[2] and Ost.[3] Inasmuch as we were working with an entirely different object in view, the conclusions reached were in no way influenced by the conclusions reached by the above writers.

While making an examination of a large number of saccharine products, the writers were led to believe from certain results that complete inversion could be effected by means of acetic acid. This view was contrary to the general opinion of chemists, although as prominent ones as Jungfleisch and Grimbert[4] claim that acetic acid completely inverts sucrose at 100°, and that it is preferable to other acids, since its presence is without effect upon the levulose of invert sugar. This conclusion was reached from the fact that the specific rotatory power of pure levulose corresponded almost exactly with that of levulose calculated from invert sugar, the inversion being effected by acetic acid. Hydrochloric acid gives a higher invert reading, because, in some way, it acts upon the levulose and increases very percepti-

[1] Boh. Zeit. Zucker, Ind., *1891*, 187. Bull. Assoc. Chim., *1892*, 559.
[2] *Compt. rend.*, **107**, 390, and **108**, 144.
[3] *Ber. d. chem. Ges.*, **24**, 1636.
[4] *Compt. rend.*, **107**, 390.

bly, its specific rotatory power. Exceptions to this view are taken by Maumené,[1] who calls attention to the fact that the invert sugar prepared from sucrose by action of acids is not composed of equal parts of levulose and dextrose. Ost[2] not only denies that acetic acid will produce complete inversion, but also claims that it acts perceptibly upon invert sugar. Ross[3] states, as the result of a number of experiments, that it was found impossible to secure complete inversion even when ten per cent. glacial acid was used and the flask kept immersed in boiling water for forty-five minutes.

Those who claim that acetic acid does not effect complete inversion base their belief upon the fact that invert sugar, prepared by the action of hydrochloric acid upon sucrose, gives a higher reading than the corresponding solution obtained by the action of acetic acid. It was thought that perhaps acetic acid might form some compound with the constituents of the invert sugar, which might affect the reading of the polariscope. Proceeding upon this assumption, attempts were made to decompose such a compound. In the course of these experiments, which were conducted at great length, certain facts were noted which have been systematized in the following:

As stated above, Jungfleisch and Grimbert in particular, have called attention to the fact that the specific rotatory power of invert sugar, prepared by the action of hydrochloric acid on sucrose, is higher than that of the artificially made invert sugar. If, however, as Maumené claims, the invert sugar so prepared is not composed of equal parts of dextrose and levulose, then it is possible that the different readings are due to the peculiar compounds formed. In fact, one would not expect the readings to be identical under such assumptions.

Accordingly, experiments were undertaken to find out, if possible, whether the hydrochloric acid used in inversion affected in any way by its presence the reading of the invert sugar so prepared. Attempts were made in two different directions.

1. Five hundred cc. of a normal solution of sucrose (polariz-

[1] Journal des Fabricants de Sucre. Abstract from March 27, 1889.

[2] *Ber. d. chem. Ges.*, **24**, 1636.

[3] Report of the Association of Official Agricultural Chemists, Bul. 35, Div. of Chem., Dept. Agr., p. 146.

ing at 99.8) was subjected to inversion in 100 cc. flasks by adding one-tenth the volume of concentrated hydrochloric acid (sp. gr. 1.19) and heating for ten minutes, regulating the heat so that the temperature, 68°, was reached at the end of that time. These solutions were all poured into a large flask and thoroughly mixed, so as to obtain a perfectly uniform solution. Exactly fifty-five cc. of this solution were transferred to a 100–110 cc. flask, the flask filled to the mark with water, the solution thoroughly mixed and polarized. The experiment was repeated with the addition of five cc. of the same acid used in the inversion, previous to filling to the mark with water; again repeated with the addition of ten cc., fifteen cc., and twenty cc., respectively. Since the same solutions, same flasks, and polarizing tubes were used, and the temperature of the solutions did not differ more than 0.5°, corrections being introduced for this variation the chances of error in manipulation were very slight. The following readings, expressed in divisions of cane-sugar scale, were obtained for the various solutions (temperature = 20°):

Invert sugar (containing five cc. of acid)	−33.00
Invert sugar + five cc. additional acid	−33.90
Invert sugar + ten cc. additional acid	−34.65
Invert sugar + fifteen cc. additional acid	−35.60
Invert sugar + twenty cc. additional acid	−36.40

The reading is seen to increase with the addition of the acid, thus agreeing with the conclusion of Gubbe.[1] Moreover, the deviations caused by the addition of the different amounts of acid are fairly constant, varying from 0.75 to 0.95, or an average of 0.85. It was hoped that sufficiently uniform results could be obtained to allow the graphic representation, so that an estimate could be made on the effect of the original five cc. of acid added to bring about inversion. Since, however, the addition of a second, third, fourth, and fifth five cc. of acid each increases the reading of the invert sugar approximately 0.85, then we may conclude, with some probability, that the original five cc. of acid which effected the inversion would increase the reading by that amount.

2. Attempts were also made to solve the problem by neutral-

[1] *Ber. d. chem. Ges.*, 18, 2207.

izing the acid present in the invert solution by the action of sodium carbonate.

Bornträger[1] has called attention to the fact that the rotatory power of the neutralized solution is higher than that of the corresponding acid solutions. By the addition of sodium carbonate, however, not only is the acid neutralized, but a corresponding amount of sodium chloride is thereby added. Readings were taken first to find out the effect of the addition of the sodium chloride. Then, by comparing this with the variation caused by neutralization with sodium carbonate, the effect of the acid could be deduced.

Five hundred cc. of inverted sugar solution were prepared as described above. It was found that three and three-tenths grams of pure dry sodium carbonate were necessary to neutralize the acid (five cc.) present in fifty-five cc. of this solution. The experiments were conducted as in the above. Fifty-five cc. of the solution were transferred to a (100–110) flask, neutralized with sodium carbonate, the flask filled to the mark, the solution mixed thoroughly and polarized. The duplicates agreed within the limit of error in reading. The average readings on cane-sugar scale were as follows (temperature = 20°):

	Triplicates.		
	1.	2.	3.
Original solution	−33.1	−33.0	−33.20
Original solution + 3.3 grams sodium carbonate (neutral)	−33.7	−33.7	−33.85
Original solution + 6.6 grams sodium carbonate	−36.2	−36.0	−36.30

The last reading was taken in order to compare the effects of the addition of sodium carbonate before and after neutralization. It is thus seen that, while the reading of the normal solution is increased 0.6° by the addition of the necessary amount of carbonate to neutralize the acid, the subsequent addition of a like amount increases the reading 2.5°. Before ascribing this difference in reading to the effect of the acid, it is necessary to find whether or not the sodium chloride, formed by the addition of the sodium carbonate to hydrochloric acid, affected the reading.

Experiments were conducted with the same solution used

[1] Boh. Zeit. Zucker, Ind., *1891*, 187.

above. Fifty-five cubic centimeters of the solution were introduced into the 100–110 cc. flask, and the amount of sodium chloride corresponding to three and three-tenths grams of sodium carbonate, or 3.65, added, the flask filled and the solution polarized as before. The average readings on cane-sugar scale, agreeing within 0.1°, are :

Original solution	—33.1	—33.15
Original solution + 3.65 grams sodium chloride	—35.1	—35.10

Since, then, the effect of the sodium chloride was to increase the reading 2°, the acid remaining unneutralized, while the reading was only increased 0.6° by the addition of the same amount of sodium chloride, the acid being neutralized at the same time, the difference 1.4° may presumably be attributed to the action of the acid present.

This result is higher than the one deduced from the direct addition of acid given above, but it is undoubtedly the more correct of the two. It would thus seem that the acid undoubtedly increases the rotatory power, the probable increase of reading being about 1.4° on the direct scale for the normal solution.

Similar experiments were next conducted in order to find out the effect of acetic acid. The strength of the acid used may be inferred from the fact that five cc. of it required for neutralization 3.05 grams of dry sodium carbonate. The normal solution of sucrose was heated at 100° with one-tenth volume of this acid for about one hour, experiments showing that continued heating had but little effect upon the reading. By this treatment a reading for the normal solution was obtained on an average of 2° lower than when hydrochloric acid was used as the agent of inversion. The same solution which gave a reading of —33.1° when hydrochloric acid was used gave a reading of —31.1 when treated with acetic acid under the above conditions.

Experiments performed to discover whether the subsequent addition of acetic acid would affect the reading, gave the following results, on cane-sugar scale :

Original invert solution (temperature 20)	—31.10	—31.0
Original invert solution + ten cc. additional acetic acid	—30.85	—30.8

The second reading is the reading obtained from a solution exactly the same as the first ten cc. of acetic acid being introduced.

It thus appears that while hydrochloric acid increases the reading by its presence, acetic acid decreases it by a small but perceptible amount. This result agrees with Ost, who criticises the statement of Jungfleisch and Grimbert that acetic acid has no effect upon invert sugar. In order to test this further, the acid was neutralized by sodium carbonate and the difference of reading noted. This result, united with the effect due to the introduction of the sodium acetate formed, gave the means of finding the effect of the acid.

The experiments were conducted as in the above, using same solution, same flasks, and same polarizing tubes. The following are the results obtained, on cane-sugar on scale:

Original solution (temperature 20°)	−31.20	−31.1
Original solution + 3.05 grams sodium carbonate (neutral)	−32.65	−32.6
Original solution + (3.05 × 2) grams sodium carbonate	−34.80	−34.8

A marked difference is noted here as compared with similar experiments with hydrochloric acid. The neutralization of the hydrochloric acid increased the reading only 0.6°, while the neutralization of the acetic acid increased the reading over twice the amount, or 1.5°. The subsequent effects of the sodium carbonate upon the two solutions agree very well, being an increase of 2.5° in the case of hydrochloric acid against an increase of 2.2° in the case of acetic acid. This difference of 0.3° in the reading is accounted for by the fact that 3.3 grams of sodium carbonate were added in the hydrochloric acid solution, while only 3.05 grams were added in the acetic acid solution. If correction be made for this difference, the increase in readings differ only by 0.1°.

It was necessary also to find out the effect of the sodium acetate formed by the neutralization of the acetic acid by sodium carbonate. The readings on the cane-sugar scale were as follows:

Original solution (temperature 20°)	−31.1	−31.1
Original solution + 4.72 grams sodium acetate	−32.4	−32.4

The sodium acetate used was the pure anhydrous salt.

It is thus seen that while the sodium carbonate increased the reading 1.5°, the introduction into the original solution of the same amount of sodium acetate as was formed increased the

reading but 1.3°. The difference of 0.2° must be due to the presence of the acid.

The conclusion that the acetic acid by its presence lowers slightly the reading is confirmed by the fact that by the use of a weaker acid a maximum reading of —31.3° was obtained.

As might be expected the introduction of hydrochloric acid into a solution inverted by acetic acid increases the reading in a corresponding degree.

It is thus shown that the effect of hydrochloric acid upon a solution of invert sugar is to increase the reading, while acetic acid has an opposite effect. Moreover, the experiments show that the probable increase in reading due to hydrochloric acid under the conditions mentioned is 1.4°, while the probable decrease in reading due to acetic acid is 0.2°. In other words, if these two acids produced the same effects upon being heated with sucrose, there would still be a difference of reading of 1.6° due to the presence of the acid. This agrees fairly well with the actual difference observed.

In the light of these experiments it may be of interest to notice the question so often discussed, "Does acetic acid effect complete inversion?" If we suppose that no acid effects complete inversion unless it gives a reading such as that obtained by using hydrochloric acid, then most certainly acetic acid does not invert completely. If, on the other hand, we adopt as the reading of the invert solution the reading of the acid solution, corrected for the effect produced by the presence of the acid, then acetic acid gives more nearly the correct invert reading, and it is correct to affirm that acetic acid does invert sucrose completely.

Finally, the above results indicated that when Fehling's solution is used in the place of the polariscope, it would be a matter of indifference whether acetic or hydrochloric acid was used to effect the inversion of the sucrose. Experiments showed this to be true. Two solutions containing the same amount of sucrose were inverted with hydrochloric and acetic acids respectively. After inversion exactly 11.7 cc. of each solution were required to reduce ten cc. of Fehling's solution. Moreover, when Fehling's solution is used for the determination of sucrose in presence of dextrin or commercial glucose, acetic acid is preferable to hydro-

chloric acid as the agent of inversion, since the process requires no attention, and the error introduced by the hydrolysis of dextrin is less even when the most favorable method of inversion is used; *viz.*, heating for ten minutes, regulating the temperature so as to reach 68° at the expiration of that time.

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METHOD OF DETERMINING CHROMIUM IN CHROME ORE.

BY EDMUND CLARK.

Received February 8, 1895.

PROF. STORER and others have suggested the use of nitric acid and potassium chlorate as agents for the oxidation of chromic compounds to chromic acid. Using this suggestion as a basis for the determination of chromium in chrome iron ore, I have experimented with a method which has proved both practicable and accurate.

For complete analysis a half gram sample of the finely ground ore is weighed into a platinum crucible with a capacity of not less than fifty cc. The ore is covered with twenty-five grams of potassium bisulphate and fusion is commenced over a Bunsen burner with very low flame which is protected from air currents by a sheet iron chimney.

To insure complete fusion, and to guard against any loss, the operator must manipulate carefully and watch the operation from beginning to end. At first, the flame should be so low as to fuse the bisulphate very slowly.

After the mass is in a liquid condition, and there is no longer any danger of loss from spattering, the crucible is grasped with a pair of crucible tongs and the contents are run up around the sides, in order to seize hold of any particles of ore which may have become stranded there.

At this stage of the process, the flame may be increased a little so as to cause a tolerable redness of the bottom of the crucible.

At intervals of ten minutes the crucible must be manipulated by the operator as before described. Forty minutes will suffice for complete decomposition of the ore. Pour the contents into a perfectly clean and dry, four to five-inch platinum evaporating

dish, making as thin a layer of the mass as possible. Place the crucible and cover in a twelve-ounce beaker and reserve for the solution.

Cool the contents of the dish quickly by means of a shallow vessel of cold water, which should be immediately at hand. Cover the dish with a suitable watch-glass to prevent loss of particles by the sudden contraction of the cooling mass. When cool, rinse off the watch-glass and add thirty-five cc. of hydrochloric acid (1.20 sp. gr.) and twenty-five cc. of water.

Boil quietly over the flame, keeping the watch-glass on, until the solution is complete, usually requiring about fifteen minutes. Transfer the solution, with care, to the beaker containing the crucible and warm on the steam-bath until the crucible and cover can be washed free from the bisulphate fusion. The solution now occupies about 100 cc.

Let contents practically settle, then decant the clear supernatant fluid into another twelve-ounce beaker and add fifteen cc. more of hydrochloric acid to the residue. Heat on the steam-bath until nothing but silica remains undissolved. Unite solutions and filter, reserving the filtrate and igniting the filter. Weigh as silica.

The filtrate, which should be easily contained in a twelve-ounce beaker, is now rendered slightly alkaline with ammonia.

The dirty, reddish green precipitate consists of the hydroxides of chromium, aluminum, and iron. These are warmed on the steam-bath until the smell of ammonia is faintly perceptible. Filter on a fifteen cm. filter without washing and dissolve the collected hydroxides into the original beaker, with dilute hydrochloric acid. Reprecipitate with ammonia and collect on the same filter as before, washing carefully three times with hot water, combine the two filtrates, and in the united solution determine lime and magnesia by any good method.

Transfer the filter containing the precipitated hydroxides to a four and one-half inch porcelain evaporating dish and cover with a five-inch watch-glass. Add fifty cc. of nitric acid (1.42 sp. gr.) and heat gently over a Bunsen flame. From time to time carefully add potassium chlorate with a small glass or porcelain spatula. The addition of this reagent is attended with small

explosions, which should be reduced in violence, as much as possible, by adding small quantities and not too frequently. Great care should be taken here to avoid loss from spattering.

The gradual oxidation may be noticed by the changing of the dirty green color of the emulsion to a clear orange-red solution. The organic matter of the filter-paper has been completely oxidized along with the chromic hydroxide. The complete oxidation is easily detected, but a small excess of potassium chlorate is added to insure it. The chromium now exists as chromic acid.

Transfer the solution to a twelve-ounce beaker, making up to about 150 cc. with water, and precipitate the iron and alumina with ammonia. Filter into a sixteen-ounce beaker without washing. Dissolve the precipitate on the filter with warm, dilute nitric acid and wash thoroughly, allowing the solution to run into the beaker in which the precipitation was made. Reprecipitate with ammonia and throw the precipitate on the same filter, allowing the filtrate to be caught in the same beaker as was the first filtrate. Separate, and determine, the iron and alumina by any good method.

The ammoniacal filtrate contains the chromium as ammonium chromate. Acidify with hydrochloric acid and add a sufficient quantity of strong sulphurous acid water to completely reduce the chromium. The clear, bright green color imparted to the solution is an indication of the complete reduction.

The excess of sulphurous acid must be driven off. This may be done by boiling, but it may be accomplished in a highly satisfactory manner by leaving the open beaker remain on a steam-bath over night.

Upon the complete removal of the sulphurous acid, the solution is rendered just alkaline with ammonia, with a final addition of three or four drops in excess. Stir well with a glass rod and heat over a lamp until the smell of ammonia is only faintly perceptible. We have, now, a precipitate of chromium hydroxide ready for filtration. Filter on a 12.5 cm., filter and allow it to drain without washing out the beaker or washing the precipitate. After the precipitate has drained, wash it carefully back into the beaker by inverting the funnel and using warm water. Add more warm water and stir to insure complete solution of all alkaline salts.

Throw the precipitate back upon the same filter and wash three times with hot water. Drain, dry, and ignite in a platinum crucible and weigh as chromium sesquioxide.

Another method of determining the chromium in the yellow solution of ammonium chromate, and one which many chemists may consider the more expedient, is as follows:

Moderately acidify the ammonium chromate solution with acetic acid and warm. Add an excess of a clear solution of plumbic acetate and allow the precipitate of plumbic chromate to settle in a warm place for several hours; then collect on a weighed filter (previously dried at 100° C.) and wash with cold water.

Dry at a temperature of 100° to 110° C. and weigh. The increase of weight is the weight of the plumbic chromate, from which the percentage of chromic oxide may be calculated.

The choice given to either of these methods for the final precipitation of chromium is purely arbitrary.

In a future article the method employed in the estimation of chromium in chrome steel and ferro chrome will be dealt with.

NEW BOOKS.

PROCEEDINGS OF THE ELEVENTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, BULLETIN No. 43, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY, EDITED BY DR. H. W. WILEY. pp. 403. Washington: Government Printing Office. 1894.

This bulletin issued annually through the courtesy of the U. S. Department of Agriculture, contains, as usual, the results obtained by the various reporters appointed by the Association, a general discussion of their reports, and a complete summary of the methods of agricultural chemical analysis which are now almost universally used in this country and which have official recognition.

Some sixty chemists participated in the meeting, and the very full discussions denote a lively interest in the work. For the first time a committee was appointed to consider the changes of method recommended by the various reporters and to approve the same before submitting them for action. Most of the changes recommended were approved by the committee. It is, however, gratifying to note that these changes were, as a rule, unimpor-

tant. The analyses made for nitrogen by the official methods agree closely and the only change made was in the wording of the Gunning method modified to include nitrates. The Tiemann-Schulze method for nitrates alone, was adopted as a provisional method until a better could be found although the reporter was instructed to continue his efforts in this direction. The use of two and five-tenths per cent. acid and alkali was dropped from the method of crude fiber determination leaving the one and one-fourth per cent. solution alone official. The dilute ammonia for washing magnesium pyrophosphate was made more definite in strength by prescribing a two and five-tenths solution, and Pemberton's volumetric method for estimating phosphoric acid appears quite promising and bids fair, after further study, to become official. No co-operative work was done on dairy products either from satisfaction with our present methods or from lack of interest. One or two changes in the methods for potash were made for the sake of uniformity. The report on soil and ash analysis was quite full and an unusually large number of chemists took part in the investigation. This is the more surprising as the analyses are very tedious and a large outlay of time was necessary. The results too are unsatisfactory both on ash and on the soil solutions, in view of which the question may well be raised as to how our general methods of mineral analysis would compare in the hands of different analysts. The changes of method adopted for soil analysis have already been printed in this JOURNAL, **16**, 792. One noteworthy point brought out by the reporter as a result of his work and that of other chemists is that the best glass is fully as good as the best porcelain for the solution of silicates and that no appreciable error will be introduced by its use. A reporter on tannin was appointed for next year and provisional methods adopted. The reporter on fermented liquors was also instructed to include the analysis of distilled liquors in his next year's investigations. Nearly 150 pages of the bulletin are covered with abstracts of agricultural chemical articles and represent the year's work of the abstract committee.

There seems to be a growing conservative feeling among the members in regard to alterations of method as a result of some

past mistakes. This is to be commended but should not be carried so far as to become prohibitive. The best results will be reached when good judgment and conservatism go hand in hand. Many will doubt the wisdom of the change made in the constitution itself, prohibiting any change, except by unanimous consent, in the methods of fertilizer analysis until an opportunity shall have been given all official chemists to try the same. This gives to any one member a power to delay action which many will think should be held by the majority alone. The appointment of reporters for two years, and associates who shall fit themselves to become reporters on the special lines of work, should meet the approval of all chemists and may be far-reaching in its results. The Secretary of the Association has not felt himself impowered to make any alterations whatever in the wording of the methods; and it is pleasing to learn that a special committee has been appointed to rewrite the methods and put them in creditable English.

There is a growing feeling in the Association that it is reaching the point where it can well enlarge its scope. In the past it has confined itself strictly to analytical processes, but the desire seems to be increasing for investigations along the line of availability in fertilizer and food material and to make more of a study of proximate constituents. General dissatisfaction is expressed with the present "citrate-soluble phosphoric acid," "crude fiber," "nitrogen-free extract," etc., and it is to be hoped that dissatisfaction will lead to renewed investigations. The Association has an additional and unlimited field of usefulness for itself along this line.

C. L. PARSONS.

BIBLIOGRAPHY OF ACETO-ACETIC ESTER AND ITS DERIVATIVES. By PAUL H. SEYMOUR, M.S., INSTRUCTOR IN CHEMISTRY, LAKE FOREST UNIV. Smithsonian Miscellaneous Collections, No. 910. pp. 147. Washington: Smithsonian Institution. 1894. Price 75 cents.

The rapidly increasing literature of aceto-acetic ester makes this volume of great value. The author has given brief abstracts of the articles that have appeared upon the subject of the bibliography from 1840–1891, "omitting what had no relation to aceto-acetic ester." The abstracts are clear, and full enough to

accomplish their time-saving purpose. Misprints are infrequent. On page 107, however, we find "uvitic acid" and "carbuvitic acid" instead of uvic acid and carbuvic acid. Excellent author and subject-indexes accompany the abstracts.

L. B. H.

REPORT ON THE EXTENT AND CHARACTER OF FOOD AND DRUG ADULTERATION, BULLETIN NO. 41, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY. BY ALEX. J. WEDDERBURN. pp 64. Washington: Government Printing Office. 1894.

EIGHTH ANNUAL REPORT OF THE DAIRY AND FOOD COMMISSIONER OF OHIO. BY F. B. MCNEAL, COLUMBUS, OHIO.

FIRST ANNUAL REPORT OF THE COMMISSIONER OF AGRICULTURE OF NEW YORK. BY F. C. SCHRAUB, ALBANY, N. Y.

A COMPILATION OF THE PHARMACY AND DRUG LAWS OF THE SEVERAL STATES AND TERRITORIES, BULLETIN NO. 42, U. S. DEPARTMENT OF AGRICULTURE, DIVISION OF CHEMISTRY. BY ALEX. J. WEDDERBURN. pp 152. Published by order of Congress. 1894.

There seems to be a growing interest among our legislators and among the general public in reference to pure foods and drugs. Many of the states and, in fact, a majority have laws making druggists responsible for the drugs they sell, requiring that only pure dairy products shall be sold, and placing a standard on commercial vinegar, but in most instances the laws have simply served to adorn the statute books. Much work has been done to arouse the public, and in view of the strict control exercised on adulteration in most other advanced countries, it is surprising that it has not met with more immediate success. The cause has undoubtedly been injured by grossly exaggerated articles claiming general impurity of all our food products, but enough adulteration, proved by actual analysis by competent chemists, is now coming to light to demand immediate enlargement and enforcement of our laws.

The chief records of recent opinions and analyses will be found in the above reports. Among the replies received by the special agent of the Department of Agriculture and recorded in Bulletin No. 41, will be found many statements by some of our best chemists. These are, in general, noteworthy for their conservative tone but, as a rule, each has had some form of adulteration come under his personal notice, and those whose duties have caused them to investigate the matter, give many examples of foods,

drugs, and dairy products, which they have found badly falsified.

It seems to have been left, however, for the Food and Dairy Commissioner of Ohio to make the first really important move in this matter, and the results tabulated in his Eighth Annual Report make extremely interesting data for chemists at large. It is true that in Massachusetts, New York, Wisconsin, and a few other states, a good many cases have been prosecuted for violation of the laws, but the examination of food products have been made mainly to prevent the watering and skimming of milk and the substitution of oleomargarine for butter. In Ohio, however, there is a much broader clause in the law, to the effect that "any article made of or sold under the name of another article, or falsely branded, or upon which art has been used to conceal inferiority, or in which there is fraud or deceit," shall be deemed illegal. Upon this basis the efficient Commissioner, Mr. F. B. McNeal, appears to have attempted, without fear or favor, to purify the food stuffs of all kinds sold within his jurisdiction. His work has been eminently successful, the results are widely quoted, and several states are apparently about to appoint Commissioners to follow his example. Among the substances found adulterated, baking-powder, buckwheat flour, butter, cider, coffee, chocolate, condensed milk, fruit-butter, honey, jelly, oleomargarine, olive-oil, preserves, quinin pills, vinegar, and wine, were impure in at least half of the samples analyzed, and in some cases there was not a particle of the substance itself present. Other noteworthy examples of impurity were in pepper, milk, mustard, cream of tartar, etc., and it will be specially interesting to note that butter added to oleomargarine is considered also in the light of an adulteration. The analyses are printed in more or less detail and will be useful to any chemist for reference. All, however, will deplore the fact that no methods, or references to methods used, are given, and also that the word "about" is not more frequently printed to modify the results. The statement of exact percentages of butter-fat in oleomargarine, of the various impurities in coffee, of foreign fats in butter, of the water added to milk, etc., are impossible, and when so directly made are misleading to the general public and cause much trouble for conservative chemists when they are quoted against them in the

courts. With this exception there is little to criticise in the report, and it is certainly to be hoped that many others showing equal results will follow.

The First Annual Report of the Commissioner of Agriculture of New York is practically a continuation of the reports of the previous dairy commissioner. The report contains many analyses, but they are confined almost wholly to dairy products, oleomargarine, and vinegar. In the sub-report of the cheese instructor, will be found a full and detailed account of the investigations on cheese planned by Mr. Van Slyke, the chemical features of which have already been published by him in this JOURNAL, **15**, 605, 635, 645, and **16**, 712, and the Bulletins of the New York Experiment Station. One important feature of the report is the summary of the laws of all the states on foods and dairy products. From this summary it appears that the requisite standard for milk varies between twelve per cent. and thirteen per cent. solids, eighty-eight per cent. and eighty-seven per cent. water, and three per cent. to three and one-half per cent. fat, and condensed milk must be made by the evaporation of standard milk without addition of other matter. The standard for vinegar varies between a minimum of four per cent. to four and one-half per cent. acetic acid and cider vinegar must have at least two per cent. cider vinegar solids. Vinegar cannot contain any sulphuric acid, lead, copper, or other deleterious substance. In regard to oleomargarine, Massachusetts and Ohio forbid its sale if colored in imitation of yellow butter. In New Hampshire, Vermont, West Virginia, and Minnesota, it must be colored a bright pink. Pennsylvania, Virginia, Missouri, and Delaware, prohibit its sale altogether. There seems to be no detailed laws in regard to other food products.

The bulletin of the Department of Agriculture on Pharmacy and Drug Laws will serve mainly as a place of reference for legal information. Most of the states now require all persons compounding or dispensing drugs to pass rigid examinations and receive certificates of registration. Poisons are restricted in sale and must generally be labeled in red letters, and sales entered in a special poison registry book. Many of the states make the druggist responsible for the purity of the drugs he sells, while

others make him responsible only when he is aware of their character.

Altogether the four reports show a growing interest in the subject of adulteration and an increasing tendency to legislate on the subject. It would appear, however, that no general results will be obtained until there is some national law which will regulate the trade between states in adulterated goods. When such a law is passed we may soon expect an efficient control and a consequent greater field for chemical usefulness and employment. C. L. PARSONS.

KRÄFTE DER CHEMISCHEN DYNAMIK. VON DR. LUDWIG STETTENHEIMER. pp. 88. 8 vo. Frankfurt am Main: H. Bechhold. 1895. Price, 6 m.

These three lectures appear to have been held before a mixed audience, containing probably more mathematicians or physicists than chemists. They are of a polemical nature, against the molecular hypothesis, but they confine themselves to general problems and do not touch at all upon the purely chemical relations, such as those of isomerism, polymerism, and organic reactions. As far as can be extracted from a somewhat involved line of argument every substance whether a mixture, compound, or simple substance is to be regared as a homogeneous individual as long as chemical reaction does not take place. There is no separation into molecules, but every atom reacts upon every other atom in a purely mechanical way, as do the celestial bodies; atoms near one another simply influencing each other to a larger degree than those further apart. The introduction of any new atoms, whether of the same or of another sort, disturbs the equilibrium which can be restored either by an equal distribution of the new atoms throughout the mass without disturbing the relative positions of the old atoms, or by a total rearrangement of the positions.

In the discussion of the solid state, views similar to those of the late T. Sterry Hunt are developed, but they are extended over the liquid and gaseous condition as well.

All disturbances of the relative positions of the atoms are considered chemical reactions, whether these be performed by simply separating them mechanically, as in pouring half of a liquid into another vessel, or by what are ordinarily known as chemical changes or, by electrolysis, change of aggregation, etc. The

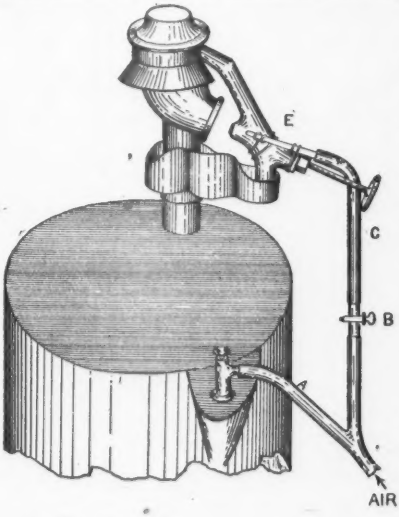
various modes of energy are all considered to depend exclusively upon relative changes of position between the atoms. Such views as those of Williamson's hypothesis are discarded because atoms are not even momentarily associated into real molecules.

It is difficult to criticise the reasoning, inasmuch as it is based upon the most general forms of phenomena and deals with these in the largest possible fashion, dealing with infinitesimal disturbances in very large masses. Until the subject is applied to purely chemical reactions in greater detail no gain can be perceived in these new assumptions. The grounds upon which the molecule, as a physical identity, is abandoned, appear to be somewhat trivial.

M. L.

NOTES.

An Improvement on the "Dangler's Laboratory Lamp."—The enclosed sketch illustrates an improvement on the "Dangler's Laboratory Lamp." After using this lamp for about two years it began to burn with a smoky flame. I then introduced a small jet of air into the flame as shown. By the help of the glass stop-cock the air is regulated, while a steady pressure is exerted on the gasoline through the side tube A. In this way the lamp will burn all day with a uniform and most perfect flame, strong or weak, as desired; no gas-burner can possibly give better satisfaction.



B. Glass stop-cock.
C. Rubber tubing.
E. Glass tip kept in place by a copper wire.

The air-blast is obtained from a Bunsen filter-pump, which is supplied with water from an artesian well.

ANDREW LUNDTEIGEN.

Spurting in Cupellation.—Dr. H. G. Torrey, of the N. Y. Assay Office, writes to the *Engineering and Mining Journal*, under date of February 26, that a comparative test of old and new cupels has been made with reference to their liability to spurt and thereby cause loss in the muffle. The test was made on 1,000 each of cupels less than one week old and about one year old. "In each case the number of cupels that spurted was the same, being only about one per cent. * * * The result of all the different experiments [which we have made] is that the spurting is due not to moisture, but to the escape of gas arising from the decomposition of impurities remaining in the cupel, and that this gas not only takes time but a high heat to expel."

A Substitute for Hydrogen Sulphide is found by Schiff and Tarugi in thioacetic acid made by acting on glacial acetic acid with phosphorus pentasulphide. The solution, for students' use, is made by dissolving the acid in a slight excess of dilute ammonia, and is given out in bottles having a pipette holding about two cc. thrust through the cork. About one-half to one gram of substance, dissolved in hydrochloric acid, is treated, while hot, with one and one-half to two cc. of a thirty per cent. solution of the above ammonium thioacetate. The sulphides are completely separated; even arsenates are completely decomposed. *Ber. d. chem. Ges.*, **27**, 3437.